

January, 1933

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME VI

NUMBER 1



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RUBBER CHEMISTRY AND TECHNOLOGY

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No. 1

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Correction

In the article entitled, "Studies on the Combined Use of Two Different Accelerators," by Minatoya in the October, 1932, issue of RUBBER CHEMISTRY AND TECHNOLOGY there are on page 658 three photomicrographic reproductions which read consecutively from left to right: "Mercaptobenzothiazole," "Diphenylguanidine," "Molecular compound."

These should read consecutively "Mercaptobenzothiazole," "Molecular compound," "Diphenylguanidine," *i. e.*, the middle illustration is of Molecular compound and the right hand illustration is of Diphenylguanidine.

C. C. D.

New Books and Other Publications

Methods of Test Relating to Electrical Insulating Materials. Report of Committee D-9. American Society for Testing Materials. 1932. 236 pp. \$1.25.

This publication contains the extensive 1932 report of A. S. T. M. Committee D-9 on Electrical Insulating Materials and all the standard methods of testing insulating materials that have been developed by the Society. There are 29 standards included, of which 18 are test methods promulgated by Committee D-9, 10 are specifications covering rubber and textile products used in the electrical industry, and one is a method of testing the insulating qualities of slate.

Several of the test methods are new ones, accepted by the Society this year covering laminated tubes, laminated round rods, flexible varnish tubing and pasted mica. The tests for dielectric strength of sheet and tape materials and for power factor and dielectric constant of insulating materials are included in their revised form. Revised specifications for friction tape for general electrical purposes and rubber insulating tape are given. [From *The Rubber Age* of New York.]

Annual Report of the Director of the Bureau of Standards. Published by Department of Commerce. Government Printing Office. Washington, D. C. 40 pp. 1932. 10 cents.

The activities of the Bureau of Standards extend into the field of rubber in so many directions that any report of this governmental agency is bound to have some interesting reference to work pertinent to the industry. For instance, in the last year a study of sounding, pilot and ceiling rubber balloons used in the Weather Bureau resulted in improved life and quality and provided data for calculating the performance of the balloons in the upper atmosphere. This is only one of the interesting studies made by the Bureau touching upon the rubber industry. [From *The Rubber Age* of New York.]

National Directory of Commodity Specifications. Bureau of Standards. U. S. Department of Commerce. 1932. 548 pp. \$1.75 Second Revised Edition.

In it are listed by title, designating number, and sponsoring organization, standards and methods of test for all commodities regularly produced in this country. Each specification is also briefly summarized as to technical characteristics, scope, and special applications. These special features will aid the user of the Directory to select specifications suited to his particular needs, and will make it indispensable to all large buyers whether Federal, State, Municipal, or other.

The enumeration of standards and specifications covered in this publication is limited to those adopted by national, technical, and trade associations, and those agencies which speak with the authority of the Federal Government as a whole. The subjects and titles are grouped in accordance with a decimal system of classification, are adequately cross referenced, and are provided with a comprehensive index which facilitates rapid reference.

In the index are listed many rubber products and the national specifications adopted as standards in their manufacture. [From *The Rubber Age* of New York.]

Products of Manufacturing Industries. Census of Distribution. Fifteenth Census of the United States, 1929. Department of Commerce, Washington, D. C. 169 pp. 1932.

The report is compiled for the use of manufacturers and others, as an aid to the survey of commodity manufacture and particularly as a help in market analyses. It shows in detail the production, in quantity and value, of commodities as classi-

fied by the Census of Manufactures, as well as the number of establishments engaged in their production. The sections devoted to rubber products are especially complete and informative. [From *The Rubber Age* of New York.]

The Development of American Industries. Their Economic Significance. Edited by John G. Glover and William B. Cornell, School of Commerce, Finance and Accounts, New York University. Published by Prentice-Hall, Inc., New York. 1932. 932 pp. \$5.00.

This comprehensive work is an authoritative and adequate treatment of thirty-nine major industries in the United States. In general, each industry taken up in the volume has been treated in a similar manner, including its early history, discoveries and operations, growth of the industry and the leaders in its field, the geographical location from the standpoint of the important centers of the industry, raw materials used, manufacturing methods, important products, capital invested, and other pertinent phases of each industry.

The chapter on the rubber industry by A. C. Grimley, of the Rubber Manufacturers Association, is especially interesting and is a comprehensive survey of the industry to the present day. [From *The Rubber Age* of New York.]

Latex Preservation and Shipment. Planting Manual No. 4. Rubber institute of Malaya, Kuala Lumpur, F. M. S., July 1932. \$2.00 (Straits).

The booklet, under the joint authorship of R. O. Bishop and R. G. Fullerton, treats the subject from the standpoint of the practical estate manager and attempts to present all available information in a concise and suitable form for those engaged in, or contemplate undertaking, the shipment of ammoniated latex under standard conditions. The book is very comprehensive and well illustrated. [From *The Rubber Age* of New York.]

International Association for Rubber and Other Cultivations in the Netherlands Indies. Eighteenth Annual Report, 1931, and the Ninth Annual Report of the Propaganda Department of the Association. Both available free upon request to the Association offices, N. Doelenstraat 5, Amsterdam.

The two reports constitute a comprehensive review of the work of the Association during the past year and contain full information on the status of the rubber industry in the Dutch East Indies at the present time. [From *The Rubber Age* of New York.]

Annual Report—Rubber Research Institute of Malaya, 1931. Kuala Lumpur, F. M. S., 1932. 134 pp. \$1.00 (Straits).

An official review of the past year's activities in Malaya during a most trying period for the rubber industry in general and research work in particular. [From *The Rubber Age* of New York.]

Die hochmolekularen Organischen Verbindungen—Kautschuk und Cellulose. (High Molecular Organic Compounds—Rubber and Cellulose.) By Hermann Staudinger, Dr. Phil., Professor and Director of the Chemical Laboratories of the University of Freiburg. Verlag von Julius Springer, Linkstrasse 23-24, Berlin W 9, Germany, 1932. xv + 540 pp. 113 figs. 17.5 × 26 cm. Price, RM. 49.60; bound, RM. 52.

It has for some time been increasingly evident that current scientific journals were becoming inadequate to satisfy Professor Staudinger's copiousness as an expositor of his own researches and speculations. The problem thus raised is solved by the book under review where, untrammelled by editorial restrictions, the author succeeds in bringing the record of his views and experimental accomplishments up to date.

In his preface Professor Staudinger states that the plan was initially to reprint all

of his previous publications in this field together with numerous new researches, but the circumstances of the times prevented the realization of this plan; and so in the present work we have the 63rd, 64th, 65th, 66th, 67th, 68th, and 69th numbered communications on high polymers, and the 38th and 39th in the series labeled isoprene and rubber. All of these are based largely on new experimental material and they bring further information concerning polystyrene, polyoxymethylene, polyethylene oxide, polyacrylic acid, rubber and balata, and cellulose. Besides this the 11th communication on isoprene and rubber is reprinted (from *Kautschuk*, 1925) for its historical value together with fresh and renovated footnotes.

The first 156 pages of the book will be of most value to the general reader since they contain a general exposition of the properties and structure of high polymers. Unfortunately, this exposition is not as concise or as well-proportioned and organized as it might be. It is in parts unnecessarily repetitious. Abandoned views of erstwhile opponents are again set forth and again re-demolished; but aside from this the contributions of other investigators are, by comparison, rather inadequately recognized. The author is inclined to be dogmatic concerning certain speculative points of interpretation where, in fact, only slender and dubious evidence is available (*e. g.*, on pp. 73 and 293 in the interpretation of the viscosity behavior of polyethylene oxides, and on p. 115 concerning the structure of balata).

It is to be hoped, however, that these comparatively minor defects and the rather excessive profusion and prolixity of Staudinger's writings will not conceal from the reader the genuine importance of Staudinger's contributions to the knowledge of macromolecular materials. There are doubtless some points on which his views will prove to be wrong, but in the main he has been consistently right even during the great revival of speculative confusion from 1924-1929 when many European writers abandoned the fundamental ideas of orthodox organic chemistry in their attempts to deal with rubber, polysaccharides, and proteins. By synthetic reactions of polymerization Staudinger provided giant molecules of relatively simple structure; he demonstrated the general structural plan of these molecules and furnished the first actual experimental material on the relation between properties and structure of linear macromolecules. The extent to which the subject of molecular colloids was clarified by Staudinger on the basis of this material is perhaps not yet generally appreciated; but there is no question that his contributions have been very important factors in the progress lately made on the structure of rubber and cellulose. They are likely to be equally significant in connection with future developments in proteins.

The most important new material in the book under review is concerned with measurements of viscosities. Staudinger's attempts to estimate molecular weights by this method have been greeted with much skepticism. He now presents a great mass of data all tending to demonstrate, in so far as it is possible to infer from the mere fact of self-consistency, that there is a simple and direct relation between the molecular weight of linear molecules and their "specific viscosities" in sufficiently dilute solutions. More astonishing is the fact that, within certain limits, the viscosity at a given concentration is determined only by the length of the polymeric chain and is practically unaffected by the presence of substituent groups or by the presence of unsaturations or other atoms than carbon in the chain (but *ad hoc* assumptions are required to bring some materials in line with this conclusion). The author states repeatedly and emphatically (*e. g.*, pp. 79, 80, 83, and 244) that linear molecules in solution are rigidly extended, but on page 130 he admits that they may bend. He no longer considers that long molecules bear free valences at the ends, or that they are rings. They are open chains with terminal groups.

The chemistry of macromolecular materials is still in its infancy and although its

growth during the past few years has been exceedingly rapid, some time must elapse before its theories are firmly enough grounded to permit the writing of a generally satisfactory textbook. Meanwhile every one interested in this field must have access to Professor Staudinger's book. Chemists generally who seek new, fresh, and spacious fields will find it a rich source of provoking suggestions for thought and investigation.

The book is beautifully printed. At the end there is a bibliography of Staudinger's papers and a subject index. [WALLACE H. CAROTHERS in the *Journal of the American Chemical Society*.]

1932 Edition-Book of American Society for Testing Materials Tentative Standards. Published by A. S. T. M., 1932. \$8.00 (cloth binding).

The Book of A. S. T. M. Tentative Standards is issued annually by the American Society for Testing Materials. Each year it includes all of the tentative standards in effect at the time of publication. The term "tentative" is applied to a proposed standard, which is given approval throughout the various steps of A. S. T. M. procedure, and which is published for one or more years to elicit comments and criticism, of which cognizance is taken before it is formally adopted and issued as an A. S. T. M. standard. Although in the trial stage, these tentative standards are in wide use due to their careful promulgation. The 1932 Book of A. S. T. M. Tentative Standards includes all of the 226 tentative specifications, test methods, definitions of terms and recommended practices effective as of October 31, 1932, including eight new standards applicable to rubber products. Specifications adopted this year for insulated wire and cable, performance rubber compound and tolerance and test methods for tubular sleeving and braids are given, among others. [From *The Rubber Age* of New York.]

"1932 Supplement to Book of A. S. T. M. Standards." American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa.

This pamphlet comprises the second supplement to the 1930 book of standards and contains 7 standards adopted or revised by letter ballot of the Society on September 1, 1932. In the present supplement 2 standards relate to metals and 5 relate to non-metallic materials. In the latter group will be found Standard Methods of Chemical Analysis of Rubber Products, and Standard Methods of Physical Testing of Rubber Products. [From the *India Rubber World*.]

"Proposed Federal Specifications." Federal Coördinating Service, Federal Specifications Board, Washington, D. C.

The following specifications, in the formative stage, are submitted to representative manufacturers for their comment and criticism.

ZZ-C-101, Rubber Catheters; No. 223, Rubber Cement for Medical Rubber Goods; No. 230b, Surgical Operating Pads; No. 231a, Rubber Pillowcases; No. 237, Stomach or Lavage Tube; No. 42, Dredging Sleeves; Friction Surface and Rubber Covered Conveyor Belting; ZZ-B-71a, Politzer Bags. [From the *India Rubber World*.]

"Rubber Covered Rolls in the Textile Industry." American Wringer Co., Inc., Woonsocket, R. I.

This booklet is on the care and protection of rubber rolls used in the textile industry. [From the *India Rubber World*.]

"The Rubber Exchange of New York, Inc." Seventh Annual Report, 1932.

In this report John L. Julian, retiring president, summarizes the activities of the Exchange for the fiscal year from September 1, 1931, to August 31, 1932. Total contracts of all classes in trading were 26,157 amounting to 258,202½ tons. De-

liveries totaled 9825 tons. The present membership of the Exchange numbers 255. [From the *India Rubber World*.]

"Foreign Commerce and Navigation of the United States for the Calendar Year 1931." United States Department of Commerce, Bureau of Foreign and Domestic Commerce, U. S. Government Printing Office, Washington, D. C., 1932. Cloth, 790 pages, 9 by 11½ inches. Indexed.

This annual statistical record presents an analytical summary of the foreign commerce of the United States in the form of tables covering kinds, quantities, and values of exports and imports; general imports; foreign merchandise in transit or transshipped; tonnage tables and tables of weight. Rubber imports, exports, and imports entered for consumption are given for the calendar year 1931. [From the *India Rubber World*.]

Chemical Engineering Catalog. Seventeenth Edition. Published by the Chemical Catalog Company, New York City. 1932. 847 pp. \$10.00.

Special effort has been exerted to interest manufacturers to include complete catalogs of their products in this volume. The section devoted to equipment is especially complete this year. The current volume contains, as usual, collected, condensed, and standardized data on equipment and machinery, laboratory supplies, heavy and fine chemicals, and raw materials with classified indices and a technical and scientific bibliography. As a reference book it finds an indispensable place in the laboratory library of rubber manufacturers. [From *The Rubber Age* of New York.]

"Worterbuch der Kolloidchemie." By Alfred Kuhn. Published by Theodor Steinkopff, Dresden, 1932. Cloth, 5 by 7½ inches, 190 pages. Illustrations and tables.

This handy little dictionary of colloid chemistry is intended for investigators in the various branches of chemistry who, while frequently meeting with colloid-chemical phenomenon, have not made a study of colloid chemistry. Among the terms listed and defined occur not only those in current usage but also such as have become obsolete. Rubber, being one of the substances considered prototypes of the colloid system, is among those receiving fuller treatment. Of special interest are the paragraphs devoted to the various types of colloid mills. The value of the work is further enhanced by numerous, clear diagrams and a bibliography. [From the *India Rubber World*.]

The Chemical Resistance of Rubber as an Engineering Material

H. E. Fritz¹ and J. R. Hoover²

Contrasting strangely with the liveliness exhibited in the physical reactions of rubber, we find in respect to chemical reactions a distinct lethargy, an inertia, which renders the material of unique value in certain engineering applications.

It is apparent, when the manifold uses of rubber as a chemically resistant material are studied, that its value in the majority of cases depends not only upon the chemical inertia and peculiar physical properties of the basic substance, but also upon the fact that this basic substance has been intelligently combined with a variety of other materials. Too much emphasis cannot be placed upon the fact that rubber compounds are designed for specific uses; and that they can be bonded to many other structural materials with practically integral adhesion.

This paper is a summary of data pertinent to the application of rubber compounds in resisting corrosion or avoiding contamination. Such data should be of service to engineers who are confronted with the selection of materials for uses where there are problems involving corrosion of equipment or contamination of product.

While unvulcanized fine Para and pale crepe rubbers have been, and to a very limited extent are still, used as corrosion-resistant linings in chemical storage, process or transportation equipment, the great bulk of rubber applied to chemical service is vulcanized. The present discussion will be limited therefore to vulcanized rubber.

When the conditions of service are accurately known by the manufacturer, vulcanized rubber can be compounded to resist actual immersion for long periods in any of the inorganic acids except those of strong oxidizing character. The same is true of nearly all inorganic salts and alkalies, and to a somewhat more limited extent of commercial organic materials.

A table has been compiled to show some of the industrial chemicals which are being successfully handled in contact with rubber. The limiting conditions of concentration and temperature for each material are shown within which the general types of rubber indicated have been found to be practically unaffected over long periods:

CHEMICAL RESISTANCE OF RUBBER COMPOUNDS

	Concentration by Weight	Maximum Temperature, Deg. Fahr.	Deg. Cent.	Degree of Vulcanization (Hard or Soft Rubber)	Design of Compound (for General Chemical Service or for Specific Service)
<i>1. Solutions of Inorganic Acids:</i>					
Arsenic acid.....	Any concentration	150	65	Soft	Specific
				Hard	General
Carbonic acid.....	Up to saturation at atmospheric pressure	150	65	Soft or hard	General
Chlorine water (hypochlorous acid).....	Up to saturation at atmospheric pressure	100	38	Soft	Specific
		150	65	Hard	Specific

¹ Manager, Chemical Sales Division, The B. F. Goodrich Co., Akron, Ohio.

² Assistant Manager, Chemical Sales Division, The B. F. Goodrich Co., Akron, Ohio.

	Concentration by Weight	Maximum Temperature, Deg. Fahr. Deg. Cent.		Degree of Vulcanisation (Hard or Soft Rubber)	Design of Compound (for General Chemical Service or for Specific Service)
Fluoboric acid.....	Any concentration	150	65	Soft or hard	General
Fluosilicic acid.....	Any concentration	150	65	Soft or hard	General
Hydrobromic acid.....	Any concentration	100	38	Soft	Specific
		150	65	Hard	Specific
Hydrofluoric acid.....	Up to 50 per cent	150	65	Soft or hard	General
Hydrogen sulfide water	Up to saturation at atmospheric pressure	150	65	Hard	General
Muriatic acid (hydrochloric).....	Any concentration	150	65	Soft or hard	General
Phosphoric acid.....	Up to 85 per cent	150	65	Soft	Specific
				Hard	General
Sulfuric acid.....	Up to 50 per cent	150	65	Soft or hard	General
Sulfurous acid (sulfur dioxide water).....	Up to saturation at atmospheric pressure	150	65	Hard	Specific
2. Solutions of Inorganic Salts and Alkalies:					
Aluminum chloride....	Up to saturation	150	65	Soft or hard	General
Aluminum sulfate.....	Up to saturation	150	65	Soft or hard	General
Alums.....	Up to saturation	150	65	Soft or hard	General
Ammonium chloride....	Up to saturation	150	65	Soft or hard	General
Ammonium hydroxide..	Up to saturation	100	38	Hard	General
Ammonium persulfate..	Up to saturation	100	38	Soft	General
		150	65	Hard	General
Ammonium sulfate....	Up to saturation	150	65	Soft or hard	General
Barium sulfide.....	Up to saturation	150	65	Soft or hard	General
Calcium bisulfite.....	Up to saturation	150	65	Hard	Specific
Calcium chloride.....	Up to saturation	150	65	Soft or hard	General
Calcium hypochlorite..	Up to saturation	150	65	Soft	Specific
				Hard	General
Caustic soda (sodium hydroxide).....	Up to saturation	150	65	Soft or hard	General
Caustic potash (potassium hydroxide).....	Up to saturation	150	65	Soft or hard	General
Copper chloride (cupric)	Up to saturation	150	65	Hard	General
Copper cyanide (in solution with alkali cyanides).....	Up to saturation	150	65	Soft or hard	General
Copper sulfate (cupric)	Up to saturation	150	65	Soft or hard	General
Ferric chloride.....	Up to saturation	150	65	Soft	Specific
				Hard	General
Ferrous sulfate ("copperas").....	Up to saturation	150	65	Soft or hard	General
Nickel acetate.....	Up to saturation	150	65	Hard	Specific
Plating solutions:					
Brass	}	150	65	Soft or hard	General
Cadmium					
Copper					
Gold					
Lead					
Nickel					
Silver					
Tin	}	150	65	Soft or hard	General
Zinc					
Potassium cuprocyanide	Up to saturation	150	65	Soft or hard	General
Potassium dichromate..	Up to saturation	150	65	Hard	General
Sodium (or potassium) antimonate.....	Up to saturation	150	65	Soft or hard	General

	Concentration by Weight	Maximum Temperature, Deg. Fahr. Deg. Cent.		Degree of Vulcanization (Hard or Soft Rubber)	Design of Compound (for General Chemical Service or for Specific Service)
Sodium (or potassium) bisulfite.....	Up to saturation	150	65	Hard	General
Sodium (or potassium) acid sulfate.....	Up to saturation	150	65	Soft or hard	General
Sodium (or potassium) chloride.....	Up to saturation	150	65	Soft or hard	General
Sodium (or potassium) cyanide.....	Up to saturation	150	65	Soft or hard	General
Sodium (or potassium) hypochlorite.....	Up to saturation	150	65	Soft Hard	Specific General
Sodium (or potassium) sulfide.....	Up to saturation	150	65	Soft or hard	General
Sodium (or potassium) sulfite.....	Up to saturation	150	65	Soft or hard	General
Sodium (or potassium) thiosulfate.....	Up to saturation	150	65	Soft or hard	General
Silver nitrate.....	Up to saturation	150	65	Soft Hard General	Specific if discoloration is to be avoided
Tin chloride (either stannous or stannic).....	Any aqueous solution	150	65	Soft or hard	General
Zinc chloride.....	Up to saturation	150	65	Soft or hard	General
Zinc sulfate.....	Up to saturation	150	65	Soft or hard	General
3. Organic Materials:					
Acetic acid.....	Any concentration	150	65	Hard	Specific
Acetic anhydride.....	150	65	Hard	Specific
Acetone.....	Any concentration	150	65	Soft	Specific
Amyl alcohol.....	Any concentration	150	65	Hard	General
Aniline hydrochloride...	Any concentration	150	65	Soft or hard	General
Buttermilk.....	150	65	Hard	Specific
Butyl alcohol.....	Any concentration	150	65	Soft	Specific
Casein.....	Any concentration	150	65	Hard	General
Castor oil.....	150	65	Soft or hard	General
Catsup.....	150	65	Hard	Specific
Citric acid.....	Up to saturation	150	65	Hard	Specific
Cocoonut oil.....	150	65	Soft	Specific
Cottonseed oil.....	150	65	Hard	Specific
Dyestuffs.....	150	65	Hard	Specific
Ethyl alcohol.....	Any concentration	150	65	Soft	Specific
Ethylene glycol.....	Any concentration	150	65	Hard	General
Formaldehyde (formalin).....	40 per cent aqueous solution	100	38	Soft or hard	General
Formic acid.....	Any concentration	100	38	Hard	Specific
Furfural.....	100	38	Hard	Specific
Fruit juices.....	150	65	Soft or hard	Specific
Gallie acid.....	Up to saturation	150	65	Soft or hard	General
Glucose.....	Any concentration	150	65	Soft or hard	General
Glue.....	Any concentration	150	65	Soft or hard	General
Glycerine.....	Any concentration	150	65	Soft or hard	General
Lactic acid.....	Any concentration	150	65	Hard	Specific
Malic acid.....	Up to saturation	150	65	Soft or hard	Specific
Methyl alcohol.....	Any concentration	150	65	Soft	Specific

	Concentration by Weight	Maximum Temperature, Deg. Fahr.	Deg. Cent.	Degree of Vulcanization (Hard or Soft Rubber)	Design of Compound (for General Chemical Service or for Specific Service)
Mineral oils.....	100	38	Hard	General
Olive oil.....	150	65	Hard	Specific
Propyl alcohol.....	Any concentration	150	65	Soft	Specific
				Hard	General
Soaps.....	Any concentration	150	65	Soft or hard	General
Sweet milk.....	150	65	Hard	Specific
Tannic acid.....	Up to saturation	150	65	Soft or hard	General
Tartaric acid.....	Up to saturation	150	65	Soft	Specific
				Hard	General
Triethanolamine.....	Any concentration	150	65	Soft or hard	General
Vinegar.....	150	65	Hard	Specific

It should be clearly understood that the foregoing table was drawn up with the application of rubber to *chemical process equipment* chiefly in mind. For service where the requirements for long life are less severe, where slow diffusion of gas or vapor through the rubber or contamination of product through discoloration, taste or odor are not serious factors, soft rubber may often be substituted where hard is indicated; or some degree of chemical resistance may to advantage be sacrificed in the design of the compound, in order to gain certain desirable physical characteristics not otherwise attainable.

In many industrial uses rubber is thus subjected to chemical or solvent action or temperature conditions a great deal more severe than can be conservatively recommended for storage or process tank linings which must remain unaffected and adherent to the base structure for years.

Limitations

The outstanding exceptions to the general chemical inertia displayed by properly designed rubber compounds toward inorganic materials are nitric acid, concentrated sulfuric acid, chromic acid, and the dry halogens.

In the organic field, we find that rubber is swollen and deteriorated—in various degrees to be sure, depending both upon the material considered and the design of the rubber compound—but nevertheless adversely affected by nearly all liquid fatty acids, drying oils, cyclic aliphatic liquids, and aromatic solvents. Especially severe are the effects of such solvents as benzene, carbon tetrachloride, ethylene dichloride, and carbon disulfide, the latter being the worst. Mineral oils and greases seriously affect most soft rubber, but are satisfactorily resisted by true hard rubber, and by some flexible hard rubber compounds. In general, it can be stated that hard rubber is much superior to soft in its resistance to these materials.

Another serious limitation upon the use of rubber in chemical service is temperature. Above 150° F. (65° C.), the effects of oxidation, diffusion, and absorption become aggravated; and the useful life of rubber products is materially shortened under such conditions, despite all that can be done through intelligent compounding to resist these effects.

Great strides have lately been made in compounding rubber to resist the action of oils, greases, fats, and organic solvents; and to resist the deteriorating effects of high-temperature service (up to 250° F., 120° C.). It must be candidly recognized, however, that these are serious causes of deterioration even with the best of modern compounds; and that the successful use of rubber in such service depends rather upon unique physical properties of the material and the lack of better materials than upon inertness to these factors of limitation.

In discussing limitations, it is of interest to note that pure water affects rubber more seriously, especially at elevated temperatures, than do most of the solutions enumerated above. This is apparently due to molecular diffusion and is therefore markedly retarded by the presence of electrolytes.

When pure water swells soft rubber, dissolved oxygen carried into the rubber undoubtedly plays an important part in the resultant deterioration. The same is true of the rapid deterioration encountered when rubber is swollen by oils. In both cases, hard rubber is found to resist diffusion, absorption, and swelling incomparably better than soft.

Hard and Soft Rubber

Considering for the moment only the two basic materials common to all vulcanized rubber compounds, sulfur and rubber, it is a well-established fact that the resistance to chemical and solvent action, to the effects of oxidizing agents, to diffusion of gases and vapors, and to absorption of liquids is increased as more sulfur is combined in vulcanization. In vulcanizing to the hard rubber stage, moreover, we obtain greater rigidity, adaptation to certain mechanical processes such as machining, drilling, and sawing, and electrical properties not available in any other known material. At the same time are sacrificed much of the elasticity, resilience, and resistance to abrasion of soft vulcanized rubber.

The coefficient of linear expansion of true hard rubber within the temperature range 32° to 140° F. (0° to 60° C.) is from three to five times that of steel—a fact which sometimes renders hazardous the use of large size steel equipment lined with hard rubber for service where rapid changes in temperature are encountered. Hard rubber at temperatures below 32° F. (0° C.) becomes quite brittle, with consequent danger of cracking or breakage if subjected to shock.

Recent Practical Adaptations

Recognizing certain distinct advantages, and certain limitations in each type of rubber, soft and hard, for chemical service under conditions of variation in temperature, liability of shock, impact or gouging, and abrasive wear, technologists have produced a practical construction which successfully combines the two types. In this construction, a layer of hard rubber is cushioned between two layers of soft rubber, with suitably spaced overlapping expansion joints which effectively prevent cracking or buckling of the hard layer under expansion and contraction with temperature changes. Figure 1 illustrates the principle involved.

This combination can be bonded to steel and certain other structural materials and finds its chief application in lining tanks and other process equipment in chemical and allied industries.

The three-ply construction has proved remarkably immune to physical damage by shock, impact, or gouging. In addition, it combines the resistance of true hard rubber to chemical and solvent action, diffusion, and absorption, with the resilience and wear-resisting qualities of the soft rubber face layer. The relative thickness of the three plies may be varied within rather wide limits to obtain the desired properties for each type of service. Sudden variations in temperature, which are often hazardous to ordinary hard rubber linings, have no adverse effect.

It has recently been found possible, for certain types of chemical process equipment, practically to remove the temperature limitation by combining rubber advantageously with other engineering materials. For example, in a recent design of heavy duty tanks for steel pickling, where hydrochloric and sulfuric acids are used at temperatures ranging from 150° F. (65° C.) to nearly 250° F. (120° C.),

a sheathing of brick 4 to 8 in. thick protects the rubber lining not only from physical damage but from the effects of the high temperature.

Figure 2 shows a typical section through the wall of such a tank, indicating the

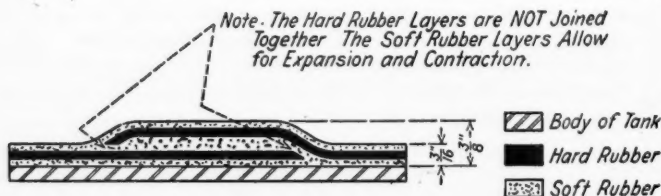


Figure 1—Three-Ply Rubber Expansion Joint

temperature drop to be expected through the brick sheathing to the surface of the rubber. This type of construction, embodying also three-ply rubber lining, represents a distinct advance in the design of pickling tanks, and opens up new markets for chemically resistant rubber. Tanks of the same general design are coming into use for the manufacture of ferric chloride, ferrous sulfate, zinc chloride, zinc

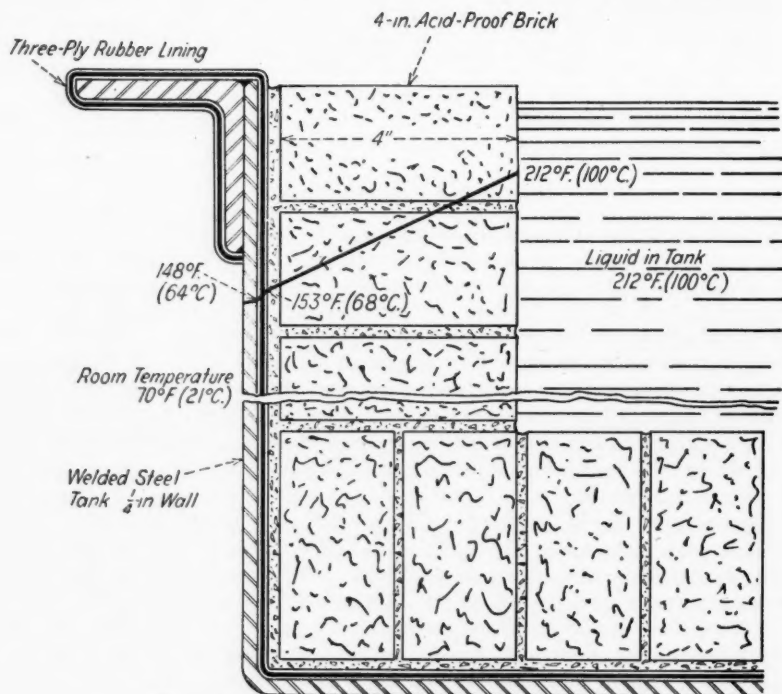


Figure 2—Temperature Gradient of Brick Insulated Tank

sulfate, and nickel sulfate; and for other chemical processes involving the use of highly corrosive materials at temperatures up to 250° F. (120° C.). Wood sheathing may replace the brick as a means of physical protection for the rubber



Figure 3—The Modern Method of Handling Hydrochloric Acid in Process Industries

Pressure discharge from rubber-lined tank car, through rubber hose, to rubber-lined storage tank. Pressure distribution through rubber-lined steel pipe from storage tank to process. Labor and maintenance costs low; no inside floor space required.

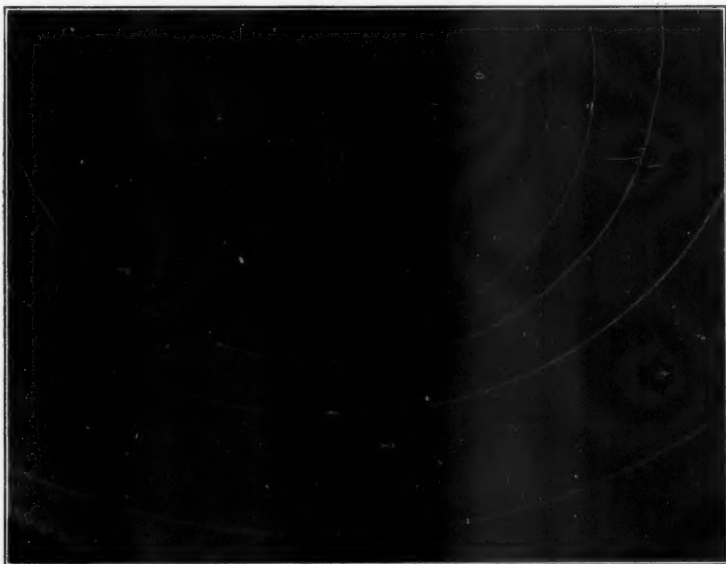


Figure 4—Interior View of One of the 32,000-Gal. Tanks. Approximately 1800 Sq. Ft. (1720 Lb.) of $\frac{3}{16}$ -In. Rubber Lining Were Used in Each Tank. Inside Dimensions, 11 Ft. in Diameter, 48 Ft. Long

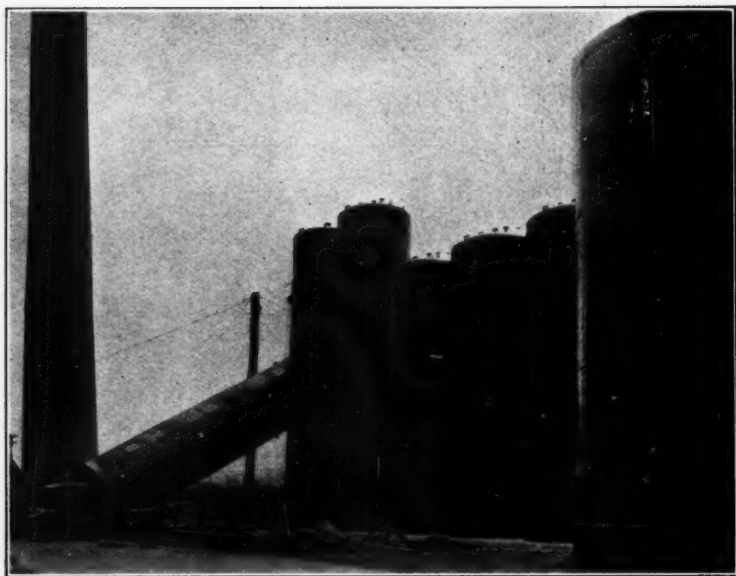


Figure 5—Erection of the Tanks. These Storage Units Are Filled from Rubber-Lined Tank Cars and Discharged under Pressure through Rubber-Lined Steel Pipe

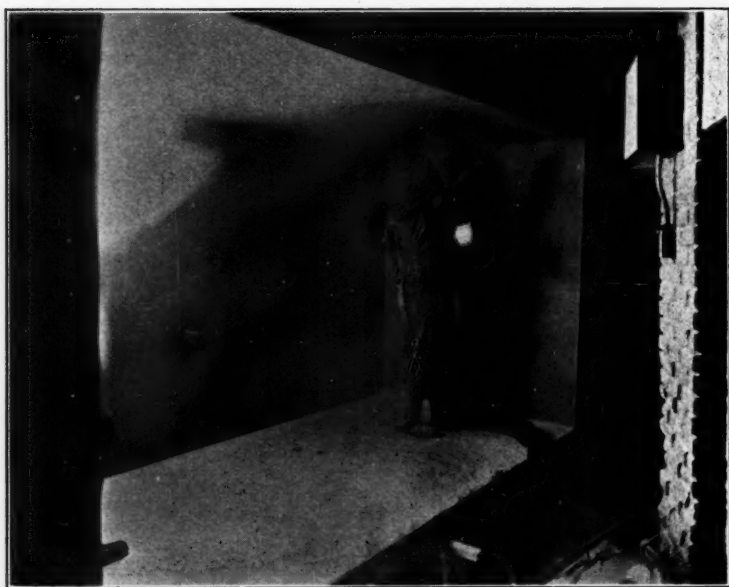


Figure 6—Sandblasting Interior of a Steel Pickling Tank in Preparation for Rubber Lining

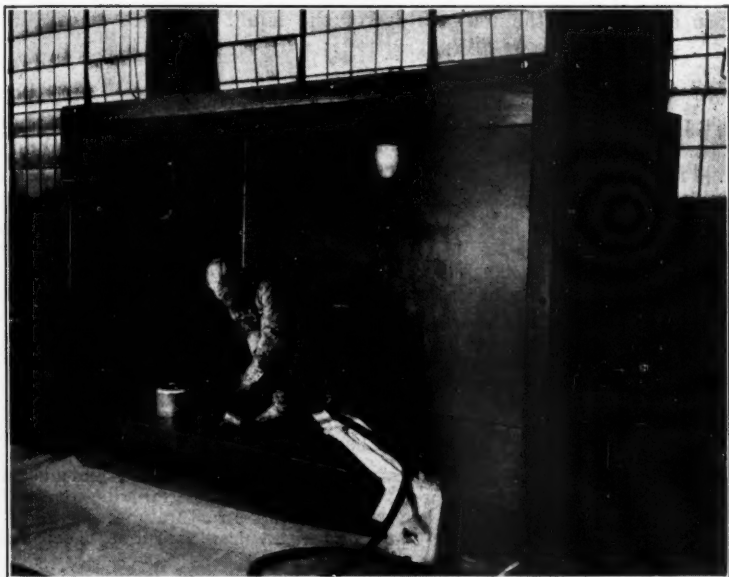
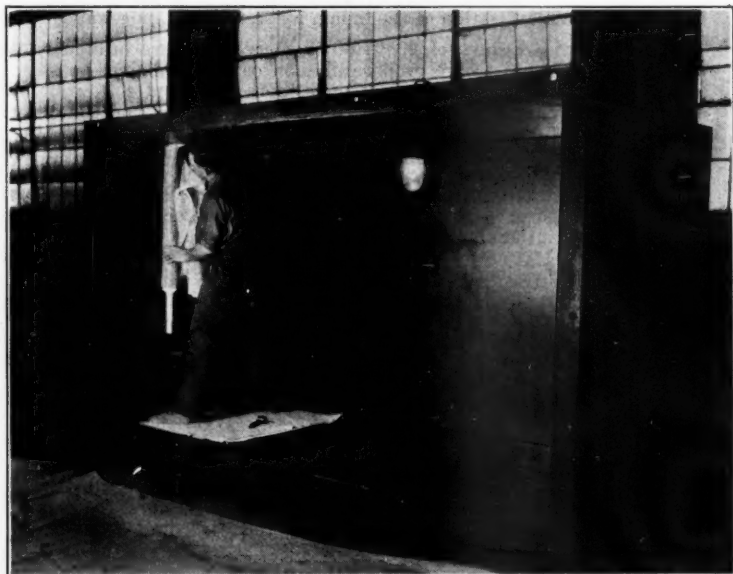


Figure 7—Application of Special Adhesive
Solvent fumes necessitate the use of gas masks during this operation.



**Figure 8—Application of Unvulcanized Rubber Lining Compound
in Sheet Form**

The lining is then rolled. Great care is required in order to insure firm contact between the lining compound and the adhesive film, and to eliminate all air pockets.

lining in cases where the temperature of the liquid does not exceed 150° F. (65° C.).

Applications

When rubber is applied to problems of industry, it is of utmost importance that the correct type of compound and the correct design of equipment are chosen. A safe rule for engineers to follow is to obtain the coöperation of reliable manufacturers with adequate technical facilities.

An outline of the major fields of present application for rubber in chemical service follows:

1. Process Equipment for Chemical and Allied Industries:

- (a) Rubber-lined tanks and tank cars (Figs. 3 to 5, inclusive).
- (b) Rubber-lined pipe, valves, and fittings.
- (c) Rubber-lined drums and barrels.
- (d) Rubber-lined pumps, fans, and blowers.
- (e) Rubber-lined rotary grinding mills.
- (f) Rubber bearings.
- (g) Rubber-covered centrifugal baskets.

For process equipment, specially designed compounds and adaptations, both hard and soft, are available. Almost integral adhesion can be secured to steel, wood, concrete, and other structural materials.

Lining steel process equipment with vulcanized rubber is accomplished briefly as follows:

- (a) Preparation of the metal surface, usually by sand-blasting (Fig. 6).
- (b) Application of special adhesives (Fig. 7).
- (c) Application of unvulcanized rubber compound in sheet form or, in special cases, by anode process (Fig. 8).
- (d) Vulcanization of the lining, by steam or boiling water.

Steam pressures of 20 to 60 lb. per sq. in. are ordinarily used to vulcanize and secure proper adhesion of rubber linings to steel. The development of lining compounds, both hard and soft, which can be fully vulcanized at the temperature of boiling water, and the study of the practical problems involved in their application, have recently made possible the lining of open tanks, towers, and other storage and process equipment too large for railroad transportation or structurally unsuited to withstand steam pressure. The three-ply construction previously described can be fully vulcanized in boiling water with adhesion to steel of not less than 500 lb. per sq. in.

2. Belting—Transmission, Elevator, and Conveyor:

For chemical mining, and in rayon and allied industries. Handling raw ore tailings and concentrates. Food industries.

Special compounds are available for handling food products without contamination. Stocks of remarkably high heat resistance have been developed.

3. Gaskets and Packing:

- (a) Gaskets for pipe couplings.
- (b) Gaskets for tanks and launders.
- (c) Packing for acid lines and corrosive gas service.

Compounds vary from pure rubber to mixtures containing high percentages of asbestos or other minerals.

4. Hose and Tubing:

- (a) Acid.
- (b) Air.
- (c) Oil.
- (d) Distillate.
- (e) Paint spray.

- (f) Grease gun.
- (g) Brewers.
- (h) Dairy and creamery.
- (i) Water.
- (j) Vinegar and cider.

In many cases it is necessary that the cover, as well as the tube—although usually of different composition in order to resist abrasion or other conditions—be resistant to the chemical in question. Practically all are soft rubber.

5. Molded Goods:

- (a) Stoppers and caps.
- (b) Battery jars, covers, and separators.
- (c) Bleach rods, bobbin holders, and candle filters.
- (d) Pipe and fittings.
- (e) Acid trays.

The compounds for the above uses vary from the softest to the hardest grades. For example, stoppers are of soft rubber and battery jars of very hard compounds.

6. Rolls:

- (a) Printers' rolls.
- (b) Paper mill.
- (c) Galvanizing and scrubber.
- (d) Cellophane.

Here, also, compounds vary depending on service, from soft to very hard.

7. Clothing:

- (a) Boots.
- (b) Shoes.
- (c) Gloves.
- (d) Aprons.

All are soft rubber compounds. They are often designed for special chemical service, such as dairies, oil fields, acid plants, tanneries, etc.

8. Sheet Rubber:

- (a) Chute lining.
- (b) Engraving gum.
- (c) Offset printing and newspaper blankets.
- (d) Flooring.
- (e) Flotation blankets and riffles.

In conclusion, it will be well again to emphasize to engineers who propose to use rubber the necessity for accurate definition of service conditions and requirements. It is only through intelligent coöperation between the engineers using rubber and the engineers designing it that the best advantage can be taken of this unique and versatile engineering material.

Water Absorption by Rubber

Part II. Vulcanized Rubber

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In a previous paper (*Trans. I. R. I.*, 7, 196 (1931)) the authors have dealt with the absorption of water by raw rubber and the work has now been extended to include vulcanized rubber.

The publications which have been made previously on the absorption of water by vulcanized rubber are not so numerous as those dealing with raw rubber. Boggs and Blake (*Ind. Eng. Chem.*, 18, 224 (1926)) and Lowry and Kohman (*J. Phys. Chem.*, 31, 23 (1927)) have demonstrated the reduction in water absorption with advancing states of vulcanization, but their work was more concerned with the mechanism of the process than the effect of fillers and accelerators.

The work of Winkelman and Croakman (*Ind. Eng. Chem.*, 22, 12, 1367 (1930)) appears to be the only published attempt to investigate the effect of state of cure and fillers on the water absorption; they concluded that (1) increased volume loading of any given filler had very little effect on the water absorption; (2) the water absorption decreased with the time of cure and reached a minimum just after optimum, after which it rose again, and (3) whiting and barytes increased the absorption by over-cured rubber, clay and zinc oxide showed the greatest increase, carbon black had little effect, whereas "Thermatomic" carbon decreased the absorption. They suggested that the increase after optimum cure might be due to a chemical change in the protein.

It has been shown by the authors in a previous communication (*loc. cit.*), that there is probably a relation between the water absorbed by raw rubber and the amount of nitrogenous material present. It was therefore decided to investigate the effect of vulcanization on the water absorption of various rubbers of known protein content to determine whether the relation applicable to raw rubber still held, and to determine the effect of (A) accelerators; (B) state of cure; (C) fillers.

Experimental

For comparative purposes three different grades of rubber were used; *viz.*, first quality pale crepe, smoked sheet, and blanket crepe.

The nitrogen content and the water absorption were determined by the methods previously described. The analytical results are given in Table I and the figures for the water absorption are reproduced graphically in Fig. 1.

It will be noted that, contrary to the usual rule, the amount of nitrogen in the particular sample of smoked sheet used was less than that in the pale crepe. It will be observed that the curves for the water absorption fall in line with the amount

TABLE I
WATER ABSORBED BY 100 PARTS OF RUBBER

No.	Sample	Protein, Per Cent	Relative Humidity (Per Cent)				
			94.9	88.6	82.6	75.5	67.7
1	Pale crepe	2.54	3.51	1.42	0.90	0.54	0.23
2	Smoked sheet	2.27	2.20	0.90	0.56	0.33	0.24
3	Blanket crepe	2.14	2.00	0.66	0.37	0.26	0.21

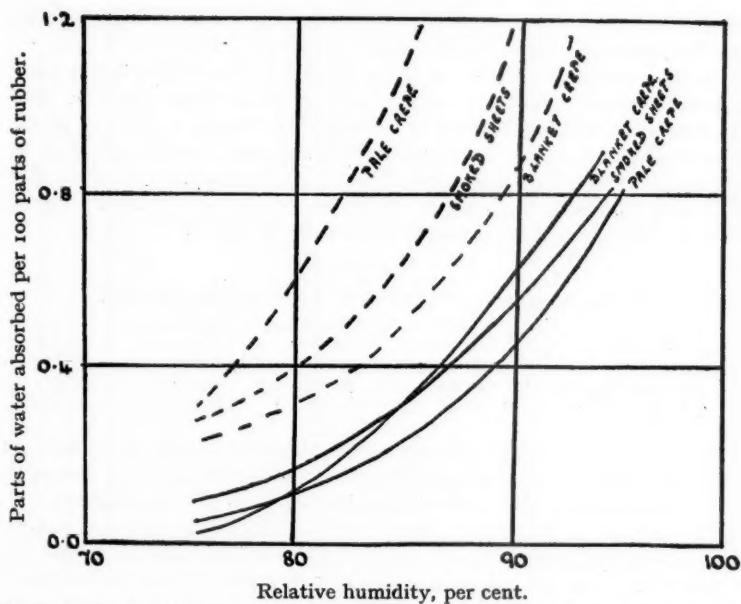


Figure 1—Water Absorptions of Raw Rubbers Contrasted with the Water Absorptions after Vulcanization

----- Raw rubber. ———— Vulcanized rubber.

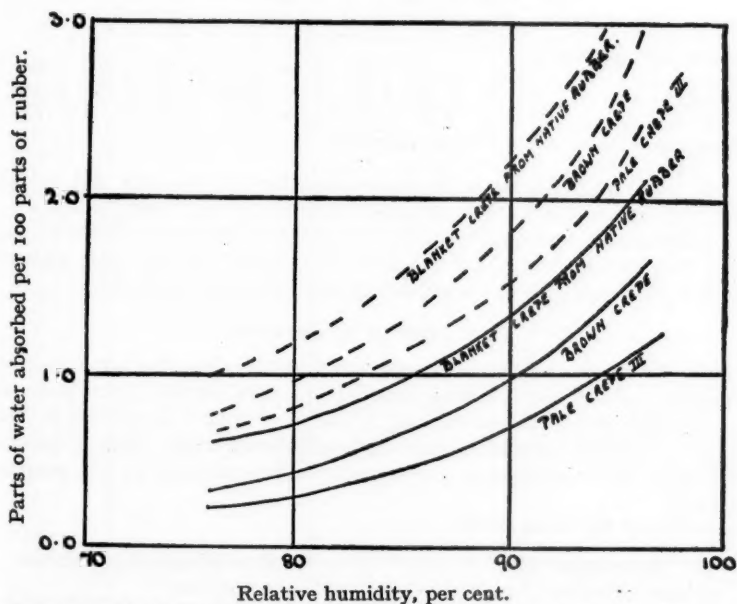


Figure 2—Effect of Vulcanization on the Absorption of Water by Samples of Native Rubber of Known Protein Content

----- Raw rubber. ———— Vulcanized rubber.

of nitrogenous material present, and it will also be noted that the higher the protein content the higher the water absorption.

In order to determine the effect of vulcanization on the rubber, a mix was made up using each sample and curing for 2½ hours at 45 lb. steam pressure. The mix used in each case contained 93 parts by weight of rubber, 3 parts of zinc oxide, and 8 parts of sulfur. The vulcanized rubber was then ground to a fine powder and allowed to stand in a desiccator for 24 hours over strong sulfuric acid. Weighed amounts were then allowed to absorb water, as for the raw rubbers. The results are given in Table II and are depicted graphically in Fig. 1.

TABLE II
WATER ABSORBED BY 100 PARTS OF VULCANIZED RUBBER

Sample	94.9	Relative Humidity (Per Cent)			75.5
		88.6	82.6	82.6	
Pale crepe	0.70	0.39	0.20	0.20	0.09
Smoked sheet	0.74	0.46	0.29	0.29	0.12
Blanket crepe	0.80	0.50	0.24	0.24	0.08

It will be observed that the curves for the vulcanized sample are close together, so close in fact that, within the limits of experimental error, they are almost identical. The absorption is also much reduced as a result of vulcanization.

In order further to investigate these results a similar experiment was carried out using inferior samples of rubber containing known amounts of nitrogenous material, and which were known to absorb water in order of their protein contents. Details of these samples are given in Table III, and Fig. 2 illustrates the results.

TABLE III

Sample	Protein Per Cent	Relative Humidity (Per Cent)							
		94.9		88.6		82.6		75.5	
		R	V	R	V	R	V	R	V
Blanket crepe from native rubber	2.3	3.29	1.97	2.49	1.30	1.48	0.85	0.99	0.59
Brown crepe	1.96	2.88	1.5	2.00	0.84	1.15	0.51	0.75	0.24
Pale crepe III	1.15	2.48	10.4	1.28	0.65	1.02	0.52	0.73	0.27

R = Raw rubber. V = Vulcanized rubber.

In this case the curves are in the same order for both the raw and vulcanized rubber, and the absorption is again much reduced by the vulcanization.

It appears that in first quality rubber the effect of the protein is not so marked as in inferior rubbers, small differences in the content having little appreciable effect on the amount of water absorbed by the vulcanized material.

(A) Effect of Accelerators

In order to determine whether accelerators would affect the amount of water absorbed by rubber, the following experiments were carried out. Three mixes were made with each of the samples (1, 2, and 3) of rubber mentioned in Table I, the mixes employed containing zinc diethyldithiocarbamate, diphenylguanidine, and litharge; and in addition a pure gum stock was prepared for the purposes of comparison.

The details of the mixes were:

(a) Diphenylguanidine	(b) Zinc Diethyldithiocarbamate
93 parts of rubber	93 parts of rubber
3 parts of zinc oxide ("White Seal")	3 parts of zinc oxide ("White Seal")
5 parts of sulfur	2 parts of sulfur
0.75 part of diphenylguanidine	0.5 part of zinc diethyldithiocarbamate

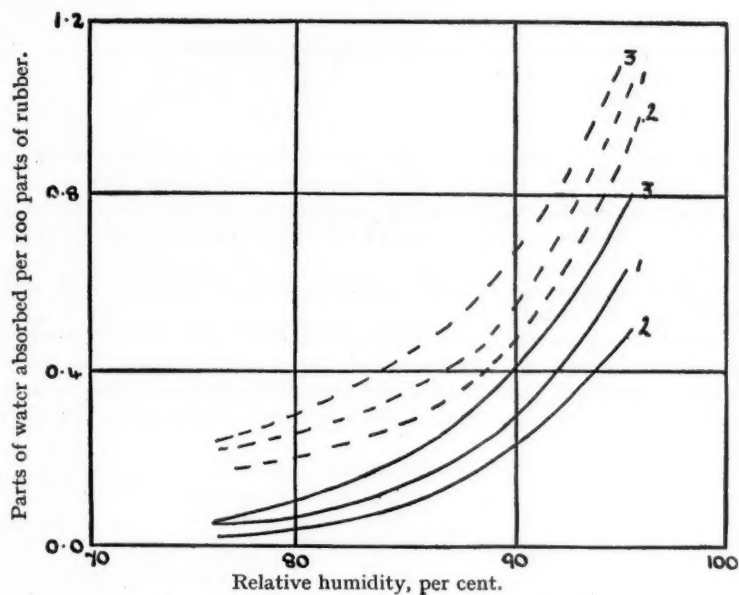


Figure 3—Water Absorption of Accelerated Stocks

----- Zinc diethyldithiocarbamate.

———— Diphenylguanidine.

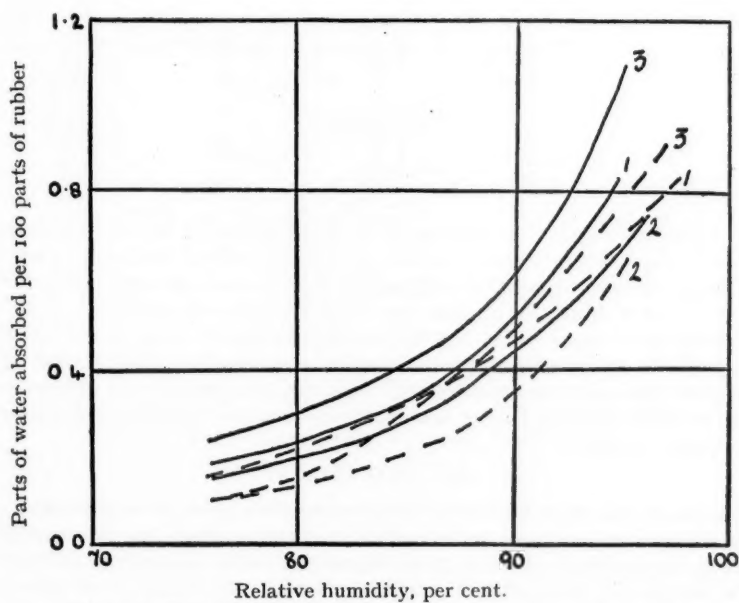


Figure 4—Water Absorption of Litharge and Unaccelerated Stocks

———— Litharge.

----- Unaccelerated.

(c) *Litharge*

93 parts of rubber
3 parts of zinc oxide
8 parts of sulfur
20 parts of litharge

(d) *Unaccelerated*

93 parts of rubber
3 parts of zinc oxide
8 parts of sulfur

For the purpose of comparison, the mix containing diphenylguanidine was made identical with that used by Winkelmann and Croakman (*loc. cit.*).

Each stock was cured to approximately the optimum cure, the times of cure being 35 min., 7 min., 30 min., and 2½ hours at 141° C. for mixes (a), (b), (c), and (d), respectively.

The water absorption was measured in the manner already described, and the results are given in Table IV.

Figs. 3 and 4 illustrate the results given in Table IV, and it will be observed that the mix containing diphenylguanidine shows the lowest absorption, and the ultra-accelerator the highest. Both the litharge and ultra-accelerator show an increase in absorption over the unaccelerated stock, whereas diphenylguanidine shows a general decrease.

TABLE IV

Sample	94.9	Relative Humidity (Per Cent)		75.5
		88.6	82.6	
Diphenylguanidine				
1	0.64	0.23	0.10	..
2	0.43	0.18	0.075	0.025
3	0.78	0.36	0.15	0.08
Zinc diethyldithiocarbamate				
1	1.05	0.45	0.28	0.20
2	0.97	0.36	0.22	0.18
3	1.17	0.67	0.42	0.23
Litharge				
1	0.85	0.45	0.25	0.15
2	0.70	0.39	0.22	0.10
3	1.10	0.52	0.30	0.22
Unaccelerated				
1	0.70	0.39	0.20	0.09
2	0.74	0.45	0.29	0.12
3	0.80	0.50	0.24	0.08

The most important effect appears to be that, instead of the absorption being in order of the nitrogen content, there is no definite general arrangement evident, the ultra-accelerator, diphenylguanidine, and litharge each give an identical order, but one different from the original and from the unaccelerated mix. The predominating effect seems to be that the sample of blanket crepe (3) now exhibits the highest absorption. In view of the different periods of vulcanization of the accelerated mixes and the unaccelerated base mix, this result is not unreasonable, as it is probable that the rubber and its components will be profoundly modified by the action of heat.

(B) *State of Cure*

Winkelmann (*loc. cit.*) stated that there was a rise in water absorption after optimum cure had been reached, and suggested that this increase was due to chemical change in the protein. In order to test these conclusions the samples in Table III were cured for five hours at 50 lb. steam pressure to ensure that they were much overcured. Their water absorption was then measured, and the results obtained are given in Table V and plotted in Fig. 5.

TABLE V
PARTS OF WATER ABSORBED PER 100 PARTS OF RUBBER

Sample	Relative Humidity (Per Cent)			
	94.9	88.6	82.6	75.5
Blanket crepe from native rubber	4.2	1.28	0.51	0.28
Brown crepe	3.8	1.1	0.50	0.22
Pale crepe III	3.35	0.98	0.52	0.21

The results show that overcured vulcanized rubber has a much higher absorption than properly cured material, but does not furnish any proof that it is change in the protein that causes the increase. If the latter were true it would be anticipated the increase would be more in the case of the higher protein rubber than in a rubber of lower protein content, and this is not the case.

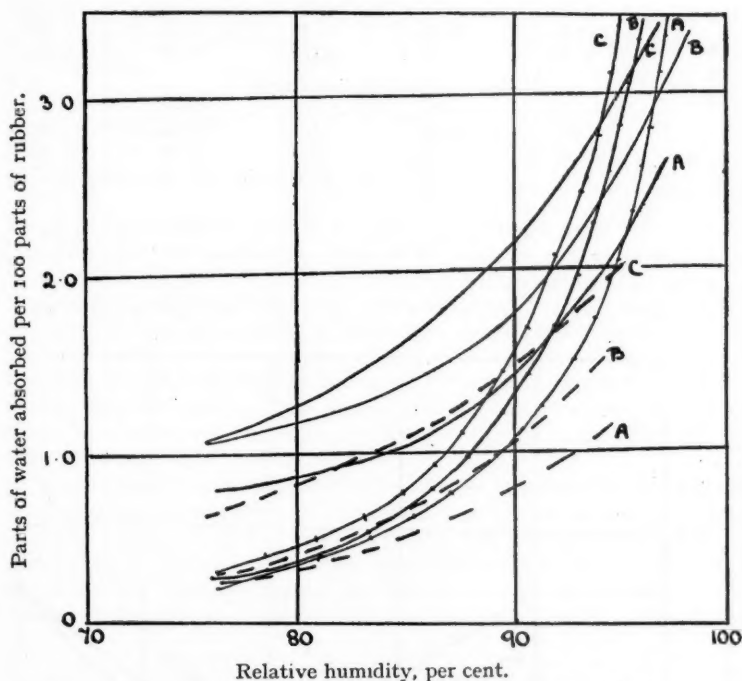


Figure 5—Effect of Overcure on the Water Absorption of Vulcanized Native Rubbers

- | | |
|-------------------------------------|-----------------------------|
| A. Pale crepe III | ----- Optimum cured rubber. |
| B. Brown crepe | ———— Raw rubber. |
| C. Blanket crepe from native rubber | + + + + Overcured rubber. |

In order to determine the effect of overcure and undercure on the stocks containing accelerators, each was cured for five different periods giving two undercures, two overcures, and an optimum, and samples of each cure were ground to a fine powder and allowed to absorb moisture from air to 94.9 per cent relative humidity. The details of the amount of water absorbed for each time of cure are given in Table VI.

TABLE VI
PARTS OF WATER ABSORBED PER 100 PARTS OF RUBBER

Sample	1 Hr.	1½ Hrs.	Time of Cure		3½ Hrs.	5 Hrs.
			2½ Hrs.	Unaccelerated		
1	0.87	0.80	0.70		0.77	0.95
2	0.85	0.83	0.74		0.80	0.95
3	0.92	0.85	0.80		0.85	1.1
Litharge						
	15 Min.	25 Min.	30 Min.		50 Min.	80 Min.
1	0.80	0.86	0.85		0.87	1.15
2	0.77	0.70	0.70		0.75	0.90
3	1.15	1.1	1.1		1.12	1.25
Diphenylguanidine						
	15 Min.	25 Min.	35 Min.		50 Min.	80 Min.
1	0.70	0.67	0.64		0.66	0.68
2	0.52	0.45	0.43		0.43	0.50
3	0.86	0.82	0.78		0.80	0.86
Zinc diethyldithiocarbamate						
	2½ Min.	5 Min.	7 Min.		20 Min.	30 Min.
1	1.06	1.05	1.05		1.08	1.35
2	0.98	0.96	0.97		1.04	1.25
3	1.22	1.17	1.17		1.25	1.45

Figure 6 shows these results graphically for the unaccelerated stock, and it will be noted that there is a gradual fall in water absorption with the time of cure, which reaches a minimum at or just after optimum, and then rises again. The other mixes give similar results, and are, therefore, not shown graphically. It

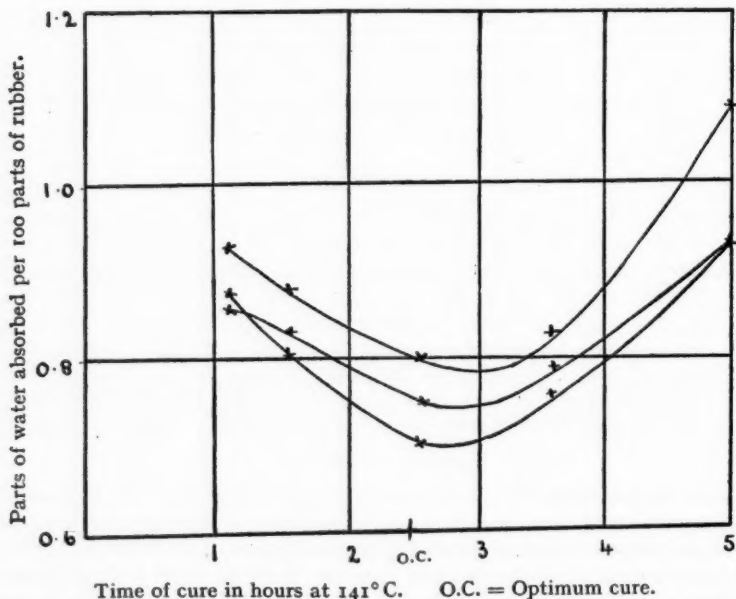


Figure 6—Effect of Time of Cure on the Water Absorption of Vulcanized Unaccelerated Stock at 94.9% Relative Humidity

appears that as a general rule overcured rubber will absorb more moisture than undercured. With regard to the individual samples and accelerators, again there does not appear to be any general order of curves for the whole series as a group, though it is worthy of note that sample 3 (blanket crepe) in all cases shows a higher absorption compared to the others than would have been predicted from its protein content and absorption as raw rubber. The mix containing zinc diethyldithiocarbamate continues to show the highest absorption whereas diphenylguanidine shows that it gives a stock the water absorption of which is rather insensitive to time of cure.

It will be noticed that in every instance the first measurement of absorption was made on a material which was not much undercured; hence it was decided

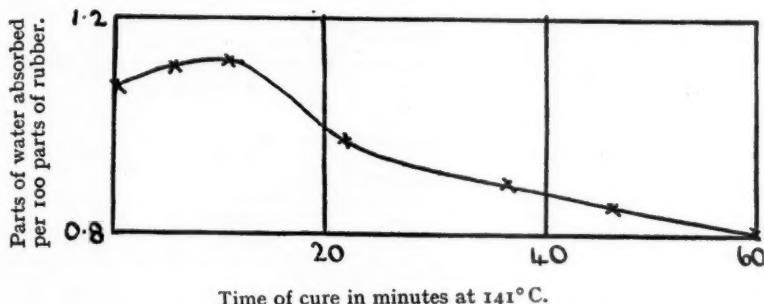


Figure 7—Effect of Undercure on Water Absorption

to investigate the earlier stages of vulcanization and to determine the effect of the first heating.

A quantity of pale crepe rubber (Sample No. 1) was masticated for 20 minutes and divided into two parts. Into one part 10 per cent of sulfur was mixed and the time of mixing noted; the other portion was then further masticated for the same time, but without adding sulfur.

This procedure was adopted in order to discover whether the incorporation of sulfur affected the absorption. It was found that on measuring the absorption of the uncured stock, with and without sulfur, that no difference in absorption could be recorded. The stock was then cured for various periods up to one hour and the undercured rubber subjected to water absorption measurement. The results obtained are given in Table VII and illustrated graphically in Fig. 7.

Time in Minutes	TABLE VII						
	0	5	10	20	35	45	60
Water absorbed at 94.9% relative humidity	1.07	1.1	1.12	0.96	0.91	0.89	0.85

It will be noted that there is a small initial rise in water absorption during the first few minutes of cure and then a gradual fall. The initial rise was observed with several different tests.

(C) Fillers

The effect of fillers was next investigated as follows, each of the mixes (a), (b), (c), and (d) had incorporated into it 15 parts by weight of carbon black, china clay ("Stockalite"), light magnesium carbonate, zinc oxide, and whiting, and portions

were cured to the optimum, and the water absorption measured. Table VIII shows the results obtained with the mix containing diphenylguanidine, and Fig. 8 shows the results graphically. The others gave similar results, and are, therefore, not reproduced. It will be observed that in general the incorporation of the filler lowers the moisture absorption while still preserving the original order of the curves. The results obtained with carbon black are interesting since they show that though the initial absorption of water at low relative humidities is higher than that of the base mix; at 94.9 per cent relative humidity there is practically no difference. This effect is only shown with the mix containing diphenylguanidine. In the case of the unaccelerated, litharge, and zinc diethyldithiocarbamate vulcanized stocks the absorption at 9.49 per cent relative humidity is lower than that of the base mix at that humidity.

TABLE VIII
WATER ABSORBED BY 100 PARTS OF MIX VULCANIZED WITH DIPHENYLGUANIDINE AND CONTAINING 15 PARTS BY WEIGHT OF FILLER

Rubber Sample	Base			
	Relative Humidity (Per Cent)			75.5
	94.9	88.6	82.6	
Base Mix with No Filler				
1	0.64	0.23	0.1	0.05
2	0.43	0.18	0.075	0.05
3	0.78	0.36	0.15	0.08
Zinc Oxide (Red Seal)				
1	0.40	0.27	0.18	0.10
2	0.30	0.22	0.16	0.07
3	0.42	0.32	0.24	0.12
China Clay ("Stockalite")				
1	0.40	0.21	0.14	0.10
2	0.30	0.18	0.13	0.10
3	0.44	0.27	0.17	0.11
Light Magnesium Carbonate				
1	0.40	0.25	0.17	0.14
2	0.33	0.19	0.12	0.08
3	0.48	0.28	0.20	0.15
Whiting				
1	0.45	0.19	0.08	0.05
2	0.42	0.20	0.10	0.07
3	0.54	0.27	0.16	0.10
Carbon Black				
1	0.69	0.53	0.41	0.36
2	0.44	0.36	0.32	0.30
3	0.79	0.60	0.46	0.33

It appears that the order of water absorption of the loaded vulcanized compounds is carbon black, whiting, light magnesium carbonate, zinc oxide, and china clay.

The amount of water absorbed by each individual filler was determined by allowing a weighed quantity of the filler to stand in a jar containing air of 94.9

TABLE IX
Percentage of Water Absorbed in 6 Days by 100 Parts of

Carbon Black	Whiting	Light Magnesium Carbonate	Zinc Oxide	China Clay
1.69	0.86	0.58	0.65	0.74

per cent relative humidity for 6 days—that being the maximum time required for equilibrium to be established, even at the highest humidities employed. The figures obtained are given in Table IX.

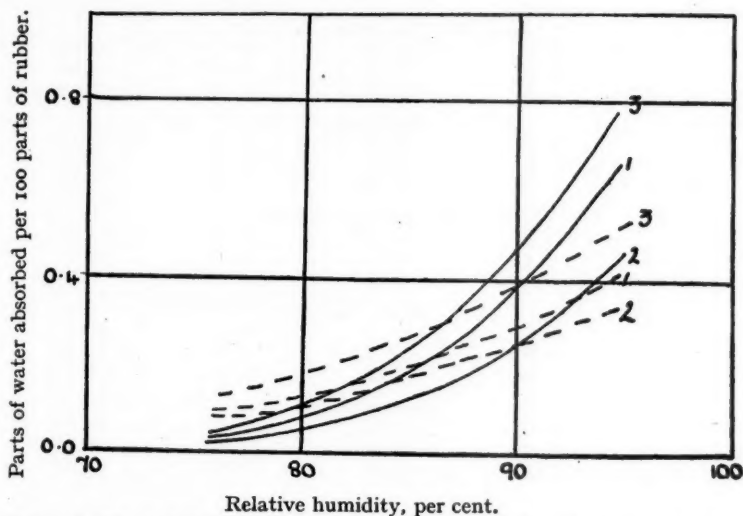


Figure 8—Effect of 15 Parts by Weight of Zinc Oxide on the Water Absorption of Stock Vulcanized to Optimum Cure with Diphenylguanidine

— Base mix. - - - Filled compound.

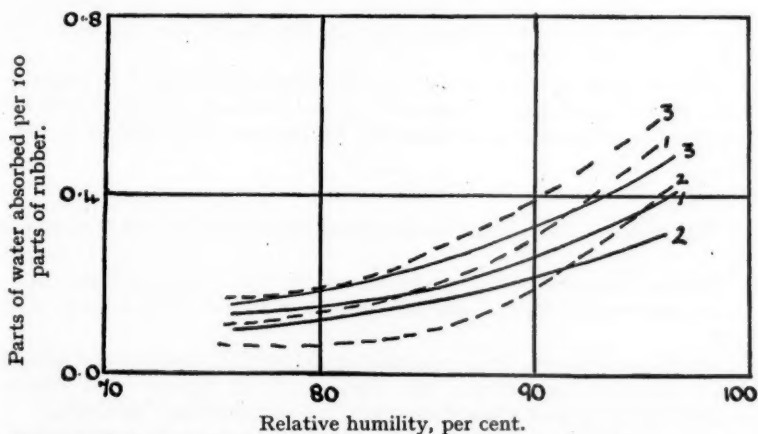


Figure 9—Effect of 5 and 15 Parts by Weight of Zinc Oxide on the Water Absorption of Stock Vulcanized to Optimum Cure with Diphenylguanidine

— 15 parts zinc oxide. - - - 5 parts zinc oxide.

The figures appear to indicate that part of the water absorbed by vulcanized rubber is due to the filler. China clay gives a higher absorption for the filler itself than would be expected from the figures obtained for the vulcanized sample containing "Stockalite."

TABLE X
WATER ABSORBED BY 100 PARTS OF VULCANIZED MIX CONTAINING DIPHENYLGUANIDINE
TO WHICH WAS ADDED 5 PARTS OF FILLER

Rubber Sample	Relative Humidity			
	94.9%	88.6%	82.6%	75.5%
	Base Mix Containing No Filler			
1	0.64	0.23	0.1	0.05
2	0.43	0.18	0.075	0.05
3	0.78	0.36	0.15	0.08
	Zinc Oxide			
1	0.53	0.27	0.15	0.10
2	0.38	0.17	0.08	0.05
3	0.56	0.35	0.20	0.15
	Light Magnesium Carbonate			
1	0.53	0.27	0.15	0.12
2	0.42	0.22	0.10	0.08
3	0.60	0.35	0.22	0.14
	China Clay			
1	0.52	0.30	0.17	0.10
2	0.36	0.21	0.12	0.08
3	0.54	0.35	0.22	0.12
	Carbon Black			
1	0.62	0.50	0.43	0.34
2	0.40	0.35	0.32	0.27
3	0.75	0.57	0.46	0.34

In order to determine whether the amount of filler present had any effect on the amount of water absorbed, the preceding experiments were repeated, using 5 parts of filler instead of 15. The results obtained are given in Table X, and typical comparative curves are shown in Fig. 9. The figures show the results for the vulcanizates containing diphenylguanidine, and it will be noted that except in the case of carbon black the stocks containing the smaller amounts of filler show the higher absorption of water.

The authors desire to acknowledge that the method employed to measure the water absorption was based on that used by the Research Association of British Rubber Manufacturers and since described by Daynes (*India Rubber J.*, **84**, 376 (1932)).

Conclusions

(1) The process of vulcanization decreases the amount of water absorbed by rubber.

(2) Rubber containing a high percentage of protein material will not after vulcanization necessarily absorb more moisture than rubber with a lower nitrogen content.

(3) Of the accelerators, diphenylguanidine induced the lowest water absorption and zinc diethyldithiocarbamate the highest. Both litharge and the ultra-accelerator showed higher absorptions than the unaccelerated base mix.

(4) After a small initial rise there is a general decrease in water absorption with time of cure. A minimum absorption is noted at, or just after, optimum cure; the amount absorbed increases again after optimum and high absorptions occur with overcured rubber.

(5) Zinc diethyldithiocarbamate shows the greatest increase in absorption with degree of overcure. Diphenylguanidine gives a vulcanizate, the absorption of which is rather insensitive to time of cure.

(6) The incorporation of fillers lowers the absorption of water.

(7) The absorption of water appears to decrease with increasing amounts of filler.

(8) Curves showing the relation of absorption to humidity, which usually appear in order of protein contents before vulcanization of the rubber, may change this order after vulcanization, but the new order will generally be maintained even after the incorporation of fillers.

The Measurement of Water Absorption by Rubber

H. A. Daynes

The absorption of water by rubber has occupied a prominent place in recent literature, especially in connection with cable and other insulating materials, since it is well known that their electrical properties are adversely affected by absorbed moisture. Many other classes of rubber goods and materials also are subject to water absorption, *e. g.*, rubber soling, tires, washers, packings, hose, tank and grinding mill linings, hot-water bottles, and surgical goods. Apart from the performance, of such articles in service, moisture absorption is important in relation to factory operations, such as drying and vulcanizing, and to storage and mechanical testing.

This paper deals with the selection of a method for measuring the amount of water absorbed by rubber when saturation has been reached. In the work for which the method was developed, the rate of absorption was of no interest; but it was necessary to correlate the water absorbed by the vulcanized product with that absorbed by the raw material, so that a method was required which could be applied equally well to raw rubber, vulcanized rubber, and ebonite.

It is not proposed to discuss in detail the mechanism of absorption. The literature has already been briefly reviewed by Lowry and Kohman (*J. Phys. Chem.*, 31, 23 (1927)), who have been largely responsible for present ideas on the subject. It will be sufficient to recall that the process is a reversible one, and that the amount absorbed at any temperature depends on the humidity of the surrounding gas and the nature of the rubber.

The increase of absorption with humidity is especially marked above 75 per cent R. H. (relative humidity); and at 100 per cent the absorption, especially with raw rubber, may continue indefinitely, so that there is no equilibrium value. Since the relation between humidity and absorption is not necessarily the same for all rubbers, it is indefinite to speak of the relative hygroscopicity of a rubber except in relation to a particular humidity.

Although a slight amount of water appears to be dissolved by the hydrocarbon according to Henry's law, the absorption at high humidities is mainly the result of the water-absorbent serum solids tending to form an infinitely dilute solution, equilibrium being brought about by the balance between the osmotic swelling pressure of this solution and the resistance of the rubber to distension.

Methods of Measurement

The principal methods available for determining absorption under definite conditions are typified by the following three methods adopted by Lowry and Kohman:

1. *Gravimetric Method in Liquid.*—Samples in sheet form are immersed in a solution of known vapor pressure, taken out from time to time and weighed after superficial drying. (This method requires only simple apparatus, but it has several disadvantages: (1) Unless the sheets are very thin (0.1 to 0.2 mm.) a long time is required to reach equilibrium; there is also some doubt as to the drying treatment required to remove the initial water content; (2) as shown by Lowry and Kohman, the absorption is complicated by oxidation unless special precautions are taken to exclude air, since oxidation may take place before sufficient time for equilibrium has elapsed; (3) the changes of weight to be measured may be affected by the removal

of sulfur or other components which bloom; (4) the removal of water-soluble components from the rubber by the immersion liquid would give low results on account of the removal of part of the original weight, the reduction in hygroscopicity of the specimen, and the reduction in vapor pressure of the immersion liquid.)

2. *Volumetric Method in Vapor*.—Samples in the form of finely cut pieces or thin sheets are enclosed in an evacuated space of known volume. Vapor is admitted in known quantities, the pressure of the unabsorbed vapor is measured by a manometer, and the weight of absorbed water is calculated by difference. (This method is no doubt the most satisfactory for accurate absolute determinations, but the use of calibrated apparatus for each specimen may be inconvenient where large numbers of samples have to be tested quickly and simultaneously.)

3. *Gravimetric Method in Vapor*.—Finely divided samples are exposed in weighing bottles to water vapor above solutions of known vapor pressure until constant weight is reached. During exposure, air is pumped out to avoid oxidation. (This method was found by Lowry and Kohman to be unsatisfactory at high relative humidities, owing to condensation of water on the weighing bottles.)

The New Method

The method now to be described is a development of Method 3 (above), but embodying one feature of Method 2, namely, that the measurements are made *in situ*, while the sample is still exposed to the controlled atmosphere. It is probably not capable of such accurate control as Method 2, but has proved convenient and sufficiently accurate for the work for which it was intended.

In principle the method consists in spreading the finely divided material on a carrier, which is then placed in a container in which the humidity of the air is controlled by a suitable salt moistened with water. At any time during the experiment the carrier and material may be weighed while still in the controlled atmosphere, or may be transferred readily to a container maintained at another humidity.

The container is a Kilner preserve jar *A* (Fig. 1), the glass lid of which is replaced by a sheet metal disc *B* with a central hole about 1 cm. in diameter. The jar is supported above the pan *C* of a sensitive balance by means of a bridge *D*. About 1 gram of the finely divided sample of rubber, etc., is spread on a watch glass *E* supported by a wire stirrup *F*, which hangs from the lower hook of the balance pan suspension and passes through the central hole of the metal disc. On the bottom of the jar is spread a quantity of the chosen salt moistened all over with water to maintain a saturated solution in contact with the air over a large area. Concentrated sulfuric acid and distilled water are used to maintain humidities of 0 per cent R. H. and 100 per cent R. H., respectively. While equilibrium is being attained and weighing operations are not in progress the stirrup is removed from the balance hook and supported by a straight rod which rests on the disc *B*, the stirrup wire resting against the edge of the hole. The central hole is then closed by a slit metal washer *H* which fits closely round the wire support to prevent diffusion of air through the hole. The metal parts are preferably made of aluminum for lightness and to avoid the danger of contamination of the rubber by copper. Temperature control is effected during attainment of equilibrium by keeping the jars in a thermostat such as a biological incubator maintained at, say, $20^{\circ}\text{C.} \pm 0.2$. The balance should be close to the thermostat and preferably at about the maintained temperature.

When it is desired to make determinations at a number of relative humidities, say, A per cent, B per cent, and C per cent R. H., the procedure is as follows: The finely cut or rasped sample is spread on a tarred watch-glass in combination with a tarred stirrup. The sample is exposed thus in a desiccator containing concen-

trated sulfuric acid and is then given a short exposure in a "zero humidity" jar. When no further loss in weight occurs, the sample and carrier are transferred to an "A per cent humidity" jar, in which they are kept at 20° C. until no further in-

APPARATUS FOR MEASURING WATER
ABSORPTION BY RUBBER AT EQUILIBRIUM

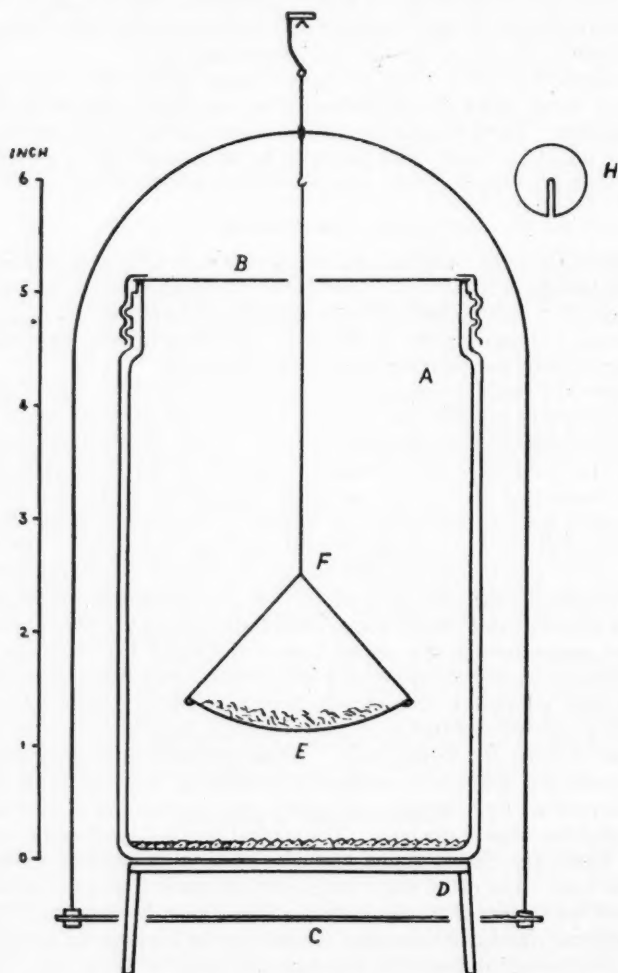


Figure 1

crease of weight occurs. This procedure is repeated at B per cent and C per cent R. H. The final increase in weight at each humidity represents the uncorrected absorption value. A correction is then applied for adsorption of water by the watch-glass and stirrup. The glass and stirrup weigh about 6-8 grams and the

corrections are about 0.2, 0.4, and 0.7 milligrams at 75.0, 84.8, and 97.2 per cent R. H., respectively. Also, as a check against accidental loss of material and in order to take account of any irreversible changes in weight due to causes other than water absorption, *e. g.*, oxidation, the samples are finally redesiccated and reweighed to see if the original dry weight is regained. An increase of about 0.1 per cent has been observed once, but this was exceptionally high.

Advantages of the Method

The above method, although similar in principle to Method 3 mentioned above, has the following advantages:

1. The material is more openly exposed to the controlled atmosphere.
2. The watch-glasses holding the material are much lighter than weighing bottles, thus facilitating accurate weighing.
3. The use of watch-glasses reduces the amount of glass surface (which adsorbs appreciable quantities of water) to a minimum.
4. For humidity control, saturated salt solutions in contact with excess of solid salt are more convenient than unsaturated solutions of salts or of sulfuric acid, because their relative humidities are not very dependent on temperature and are not affected by partial evaporation. On the other hand, intermediate humidities may sometimes have to be provided by sulfuric acid solutions or unsaturated salt solutions.
5. Weighing is carried out without removing the carrier or material from the controlled atmosphere, thus eliminating one source of error, and avoiding a break in the time curve.

A disadvantage of the method, at any rate using the apparatus described above, is that experiments cannot be made in absence of air, so that the material may be subject to oxidation. In practice, however, this does not prove to be a serious defect.

Humidity Control Solutions

It is clear from the work of previous investigators that the most interesting changes in absorption take place between about 70 per cent R. H. and 100 per cent R. H. The principal humidities chosen were 75.0 per cent, 84.8 per cent, and 97.2 per cent R. H., these being obtained with saturated solutions of sodium chloride, potassium chloride, and potassium sulfate, respectively. Leopold and Johnston (*J. Am. Chem. Soc.* **49**, 1974 (1927)) have determined the relative humidity of these solutions over a range from room temperature to about 50° C., and have shown that it does not vary rapidly over this range.

Time Taken to Reach Equilibrium from Raw, Soft Vulcanized, and Hard Rubber

The type of curve obtained when specimens of *raw rubber* were cut into shreds about 1 mm. thick, dried in a desiccator to constant weight, and then exposed to different humidities in ascending order, is shown in Fig. 2, the time being reckoned in each case from the beginning of exposure to the appropriate humidity. In accordance with the observations of previous workers it was found that no equilibrium was reached with raw rubber in a saturated atmosphere, also that there were serious difficulties even in obtaining steady readings, the weighings at 100 per cent R. H. on a sample of Sumatra smoked sheet, for example, being quite erratic.

At 97.2 per cent R. H. a sample of Hopkinson sprayed-latex rubber was still absorbing strongly after five days, but in the case of other less absorbent rubbers the

curve had become horizontal after two or three days. At lower humidities one day was sufficient for equilibrium.

As a general rule, the higher the humidity and the higher the ultimate absorption, the longer was the time required to reach equilibrium. Usually a series of exposures at three humidities, in addition to the initial and final desiccator, could be completed in 8 to 12 days, provided the room temperature was fairly near that of the thermostat, so that accurate values for the equilibrium absorption (not vitiated by humidity changes during weighing) could be obtained; with some highly absorbent rubbers, however, about a month was required.

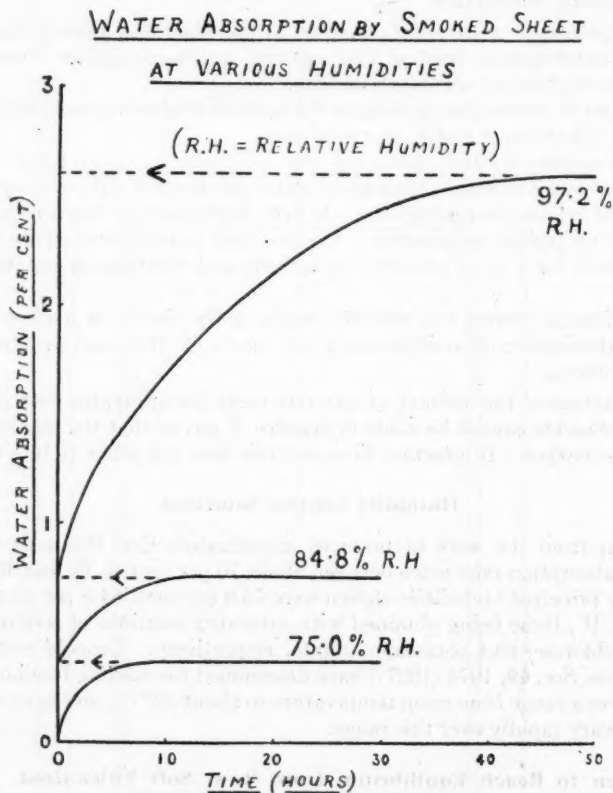


Figure 2

In the case of *soft vulcanized rubber* finely rasped samples were used instead of cut shreds. It is known that the time for reaching uniform concentration of gas through geometrically similar samples of solvent material is proportional to the square of the dimensions, so that a great reduction in the duration of test can be made by comminution.

As with raw rubber, the time required to reach equilibrium increased both with the absorptive capacity of the rubber and with the humidity. Except with highly absorbent samples at 97.2 per cent R. H., one day appeared to be sufficient for the attainment of equilibrium. Generally, the absorption with soft vulcanized rubber

was less sensitive to accidental variations under exposure conditions than in the case of raw rubber, and the equilibrium was more sharply defined.

When *hard rubber* rasped and passed through a 40-mesh sieve was tested, equilibrium was attained in a few hours, except with the most absorbent samples at high humidities. With such samples at 97.2 per cent R. H., irregular readings were obtained, as was frequently the case in experiments at high humidity, and an exposure of two or three days was necessary.

Effect of Subdivision of the Sample on Water Absorption

Apart from the obvious effect of comminution on the rate of absorption, it was conceivable that the resistance to distension of the rubber by osmotic pressure might be affected by the comminution treatment, and the water absorption thus

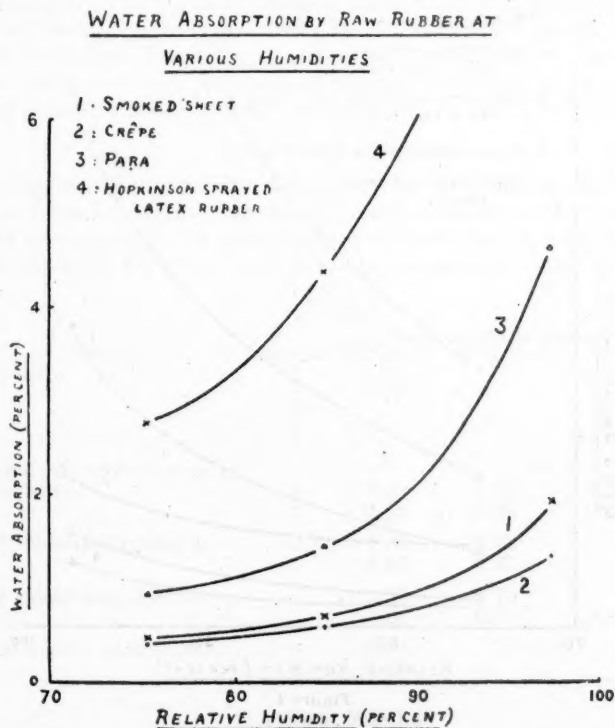


Figure 3

modified. There was also the possibility of surface adsorption. Accordingly, absorption tests were made with samples of various particle sizes. In the case of vulcanized rubber, cut and rasped samples were compared. The former gave slightly lower results, but the differences were comparable with the error of measurement. In the case of hard rubber the material was divided into portions by passing through sieves of various sizes down to 120 mesh. There was no systematic variation of absorption with particle size. It appears, therefore, that the water absorption as determined by this method is an intrinsic property of the material and is not

greatly affected by the comminution treatment. In the case of hard rubber it was decided to adopt hand-filing as standard procedure, and to use the whole of the dust which would pass a 50-mesh sieve.

Special Difficulties at High Humidities

All tests in the present work have been carried out at $20^{\circ}\text{C.} \pm 0.2$, but there is probably no serious error even if the temperature is consistently somewhat high or low. Although temperature affects the rate of absorption by vulcanized rubber, it does not greatly affect the ultimate absorption (Lowry and Kohman, *loc. cit.*).

WATER ABSORPTION BY VULCANISED RUBBERS AT VARIOUS HUMIDITIES

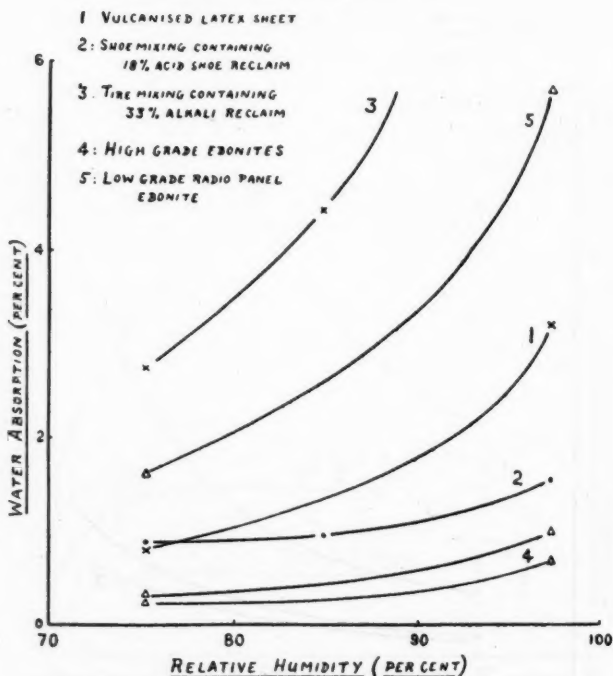


Figure 4

In the case of raw rubber the ultimate absorption is more affected by temperature (van de Leur, Delft Comm., 1917, Pt. II), but the effect of any small consistent departure from the desired temperature is in practice negligible compared with the effect of other variables the nature of which is not yet clear. At high humidities it is found that after a certain time of exposure the weight of the specimen fluctuates from day to day without showing any general increase. It is probable that this is due to slight fluctuations of relative humidity, for the humidity-absorption curve becomes very steep as 100 per cent R. H. is approached. For example, with a sample of commercial smoked sheet, Lowry and Kohman observed an increase in absorption from 2.95 per cent to 4.75 per cent for a difference of 0.9 per cent R. H.

at about 97 per cent R. H. It is probable that the fluctuations of weight could be much reduced by closer temperature control, but up to the present it has been usual to continue readings for some days after the general increase of weight has ceased, and to record the limits of fluctuation.

This difficulty is much exaggerated at 100 per cent R. H., where condensation on the sample may take place, and it is impossible then to obtain even approximately steady readings. For this reason, and because with raw rubber there is no equilibrium at 100 per cent R. H., 97.2 per cent R. H. has been adopted as a condition which gives reasonably steady results and a good indication of the behavior of the material in water or dilute solutions, such as sea water. If it is of more interest to examine the behavior of the material at some lower temperature, *e. g.*, atmospheric, another control solution should be used, so that greater regularity of results can be obtained.

The temperature of the room in which the thermostat is placed and weighing is carried out should not be very different from that at which the samples are stored but it is found that if weighing is carried out immediately on removing the jars from the thermostat there is usually no change of humidity in the jar sufficient to cause appreciable changes in weight of the specimen during weighing.

Consistency of Results

The reproducibility of results is illustrated by the duplicate and quadruplicate values in Table I. Results were usually more consistent at the lower humidities, as might be expected. No doubt more consistent results could be obtained at high humidities by the use of more accurate temperature control.

TABLE I

Material	Sample	Percentage Water Absorption at:		
		75% R. H.	84.8% R. H.	97.2% R. H.
Pale crepe.....	1	0.35	..	1.29 to 1.49
	2	0.37	..	1.52
	3	1.55
	4	1.28 to 1.43
Special pale crepe (low serum content).....	1	0.31	0.40	0.75 to 0.77
	2	0.29	0.38	0.79 to 0.80
Soft vulcanized rubber A....	1	0.56	0.62	0.92
	2	0.60	0.67	0.93
Soft vulcanized rubber B....	1	0.55	0.72	3.14
	2	0.61	0.79	3.10 to 3.31
Good quality hard rubber...	1	0.54	..	1.00
	2	0.45	..	1.01

Typical Results

A number of typical results are given in Table II and Figs. 3 and 4. Among these are data for each class of material obtained by interpolation on the humidity-absorption curves of Lowry and Kohman (L. and K.).

No direct quantitative comparison can be made between the present results and those of Lowry and Kohman, as the materials tested were not strictly comparable, but there is agreement in regard to the general features on which their theory of the mechanism of absorption is based. For example, the absorption at 97.2 per cent R. H. is much greater than at 75.0 per cent R. H. There is also a tendency for the ratio between the absorptions at 97.2 per cent, and 75.0 per cent R. H. (see last column) to be higher with the more highly absorbent samples: this

also is in accordance with the theory of water absorption, according to which if the absorption by the non-hydrocarbon portion were negligible the ratio would be about 1.3, corresponding to solution in the hydrocarbon according to Henry's law.

TABLE II
WATER ABSORPTION BY RAW AND VULCANIZED RUBBERS

	75% R. H.	84.8% R. H.	97.2% R. H.	Ratio 97.2% 75.0%
<i>Raw Rubber</i>				
Smoked sheet (L. and K.).....	0.58	0.89	2.85	4.9
Smoked sheet.....	0.45	0.68	1.91	4.2
Crepe.....	0.39	0.56	1.33	3.4
Para.....	0.92	1.43	4.62	5.0
Hopkinson sprayed-latex rubber.....	2.75	4.38	> 13.44*	> 4.9
<i>Soft vulcanized rubber</i>				
95 : 5 rubber sulfur vulcanizate from smoked sheet (L. and K.).....	0.44	0.78	2.45	5.6
Vulcanized latex sheet.....	0.79	..	3.2	4.0
Shoe mixing containing 18 per cent acid shoe reclaim.....	0.87	0.95	1.54	1.8
Tire mixing with 33 per cent alkali re- claim.....	2.72	4.41	17.9	6.6
<i>Hard Rubber</i>				
Dust, from smoked sheet (L. and K.).	0.28	0.33	0.58	2.1
High grade ebonite.....	0.24	..	0.68	2.8
Low grade radio panel ebonite.....	1.6	..	5.7	3.6

* The experiment was stopped after 14 days owing to growth of mold.

The water absorption of high-grade hard rubber is appreciably less than that of raw or soft vulcanized rubber, both at 75.0 per cent R. H. and at 97.2 per cent R. H.; so also generally is the ratio of absorption at 97.2 per cent R. H. to that at 75.0 per cent R. H. It is not possible to draw a sharp distinction between raw, soft vulcanized, and hard rubbers, owing to the wide variation in each class. These variations are of such magnitude that the comparatively large percentage fluctuations in the readings at 97.2 per cent R. H., which are sometimes observed on a single sample, do not detract seriously from the value of the method for most purposes.

The author wishes to thank the Board of Management of the Research Association of British Rubber Manufacturers for permission to publish this paper, and to acknowledge the assistance of L. H. N. Cooper and R. W. Parris, who took part in the development of the method and carried out the measurements quoted in the paper.

Atmospheric Cracks on Unstretched Rubber Products. Their Origin and Prevention

Otto Merz

BERLIN

Introduction

Technical problems can be attacked from various angles. Since it is sometimes useful to study a material from wholly new points of view, an attempt will be made in the present work to consider rubber products from the point of view of the technic of applying them as coatings. In the rubber industry rubber products are an end in themselves, whereas in the paint industry they are regarded only as a foundation on which to paint. In order to judge the possible utility of a coating an exact knowledge of the material on which the coating is applied is necessary, whether it is wood, metal, rubber, or anything else.

Formation of Cracks on Unstretched Rubber Products

The extensive experiments of van Rossem and Talen¹ show that two factors are necessary for the formation of cracks on rubber, namely, stretching of the rubber and the action of ozone. Light (sunlight or the mercury lamp) is not necessary for the formation of cracks. An oxidized film is formed by the action of light, and this film has the ability to prevent the formation of cracks. In general, cracking begins at about eight per cent elongation. In unstretched rubber no cracks are formed even at the highest concentrations of ozone. Van Rossem and Talen emphasize the fact that the formation of cracks under the influence of ozone is to be considered a characteristic property of stretched rubber. The formation of cracks in rubber articles in service under atmospheric influences is likewise to be attributed to stretching. In other words, therefore, ozone is without effect unless the rubber is stretched. In the present paper the experiments show that cracks are formed on rubber products even without any stretching and in fact the cracking may be very extensive. It should be mentioned at the beginning that in none of the experiments was the rubber stretched at all.

Technic

From four ordinary commercial samples of collapsible boat materials from well-known firms, strips 22 centimeters long and 5 centimeters wide were fastened to wooden frames made of blocks about 1.5 centimeters wide, so that the air had free access to the under sides as well.

The four samples were fastened without any stretching and without being under tension and also without any slack to two frames by three nails on each side. The upper quarter of each sample was covered with sheet metal for comparison with unweathered material. One frame was exposed at an inclination of 45° in a southerly direction (sunny side) and the other was exposed to the weather day and night about 30 meters away toward the north (shady side). Both frames were left to weather uninterruptedly day and night. The experiments were begun in June. The condition of the samples was examined after one, two, four, and eight weeks as well as after six months. Table I shows the results.

TABLE I
WEATHERPROOFING OF COLLAPSIBLE BOAT MATERIALS

Sample Number	1 Week	2 Weeks	Upper Side after Exposure of 4 Weeks	8 Weeks	6 Months	Upper Side Covered after 6 Months	Under Side (After) 6 Months
In sunlight toward the south	1 Cracking: white deposit	Cracks	Cracks	Large cracks	Weathered as far as the first ply of linen	Good (60X: good)	Good (60X: good)
	2 Good: white deposit	Cracks	Cracks	Large cracks	Weathered as far as the first ply of linen	Good (60X: small pores)	Good (60X: good)
	3 Good: white deposit	Crazing	Cracks	Cracks	Cracks	Good (60X: good)	Good (60X: good)
	4 Cracks with almost no deposit	Cracks with a little white deposit	Large cracks	Large cracks	Elephant-like wrinkles	Good (60X: isola- lated cracks)	Good Cracks
In the shade toward the north	I Good, without deposit	Good, with a little white deposit	Good	Crazing	Cracks	Good (60X: good)	Good (60X: good)
	II Good, with a little white deposit	Good, with a little white deposit	Good	Cracks	Cracks	Good (60X: good)	Good (60X: good)
	III Good, without deposit	Good, with a little deposit	Good	Good (60X: crazing)	Crazing	Good (60X: good)	Good (60X: good)
	IV Good, without deposit	Good, without deposit	Crazing	Cracks	Large cracks	Good (60X: isola- lated small pores)	Good (60X: crazing)

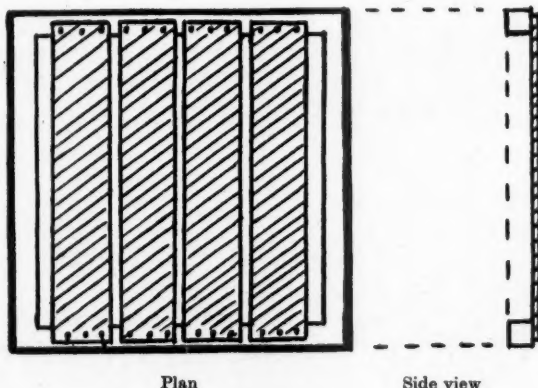
To characterize the severity of the cracking the following designations were chosen:

- (a) Good: no perceptible deterioration.
- (b) Crazing: the finest cracks visible to the naked eye.
- (c) Cracks: distinct cracks up to about 0.1 mm.
- (d) Large cracks: about 0.1 to 0.5 mm. across.
- (e) Elephant-like wrinkles. In this case the cracks had become still larger and reached the first ply of fabric, while the spaces between the cracks stood out prominently, giving the appearance of elephant hide.

At the conclusion of the experiments at the end of six months, the condition of the protected part of the samples and the under sides was examined.

In this case a more sensitive criterion was used, *viz.*,

- (a) Good even with a magnification of 60, *i. e.*, no deterioration visible under this magnification.
- (b) Good by the naked eye, but crazing visible under a magnification of 60.



Plan

Side view

Figure 1
Scale 1:1.5.

From the table it is to be seen that all the samples in the sun showed a much more rapid formation of cracks than those in the shade. On the average the results indicate that to obtain the same degree of deterioration in the shade, four to eight times as long was required as in sunlight.

The experiments of van Rossem and Talen with stretched rubber do not allow the conclusion that ozone is the cause of crack formation in the unstretched collapsible boat material. Moreover, it would be difficult to understand how the concentration of ozone, particularly in the dusty city air, would be so different only thirty meters away that the same degree of cracking in the shade would require four times as long.² It seems as if there must be still other causes not yet recognized which play an essential part in the phenomenon. Above all, the nature of the effect of light on rubber has not yet been studied sufficiently. Even if there is no cracking with mercury light, this is no definite proof, since the spectrum of sunlight differs fundamentally from the spectrum of the mercury lamp³ (Fig. 2).

Figure 3 gives the appearance of the strips after eight weeks' exposure to the sun, Fig. 4 after six months, and Fig. 5 after six months' exposure in the shade. It is

evident from these illustrations that the samples exposed for six months in the shade suffered less deterioration by cracking than the corresponding samples exposed to sunlight for eight weeks.

These results with unstretched rubber products are of course at variance with the results of van Rossem and Talen with stretched rubber mixtures containing no filler. The question then comes up, however, how far can the results on stretched unfilled rubber mixtures be compared with those on unstretched collapsible boat materials? Since van Rossem and Talen found that with unstretched rubber (without filler) no cracks appeared, it might properly be assumed that unstretched collapsible boat material would likewise have no tendency to form cracks because on the one hand the rubber content is less and on the other hand additional protection is afforded the rubber by the filler. Since this is not the case and, moreover, since the present experiments prove that stretching is not the cause of cracking, it must

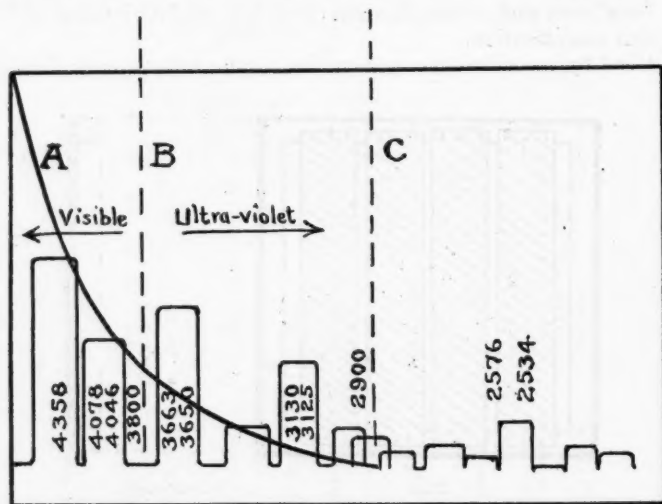


Figure 2

Wave lengths in Angstrom units; Sunlight spectrum and mercury light spectrum; A = Distribution of the solar spectrum; B = Limit of visible light; C = End of the solar spectrum at the surface of the earth; Columns = Principal spectrum of mercury light.

be that it is merely a withering effect which brings about the cracking in a similar way to the aging phenomena of drying fatty oils.⁴

With oil films as accumulators of water the rate at which swelling retracts upon aging is of greater significance, since withering follows swelling of the oil film, causing the early formation of cracks in the colored oil film. The age of the foundation oil film is also of great importance in the formation of cracks on the outer coating. According to Stern⁵ sulfur varnishes (cold and hot vulcanized fatty oils) after 5 days show a water absorption of from 5.6 per cent to 20.1 per cent. The author has as yet no information on similar investigations on factice, which is also used in collapsible boat materials. Besides the premature cracking of oil films, another form of cracking due to aging is known, and this is to be attributed primarily to physical causes, i. e., to a decrease in the elasticity of the dried-out colored layer as a result of brittleness brought on by aging.

Superficially the formation of cracks in rubber closely resembles the visible crack-

ing of oil paints (see illustrations in "Fatty Oils" by Eibner). The idea that the cracking of both these substances is due to similar causes is made more certain by the fact that upon exposure to sunlight the formation of cracks on collapsible boat materials takes place in a considerably shorter time. The idea that weathering phenomena are the cause of cracking is illustrated by two photomicrographs (Figs. 6 and 7) of material No. 4 after six months' exposure to sunlight and in the shade.

Two preliminary experiments on the action of heat and of ultra-violet light on boat materials stored for about one-half year in a room indicated a loss of weight of such material. The heat experiment was carried out for three days at 80° C. and for three days at 105° C.; the ultra-violet light experiment was carried out at a

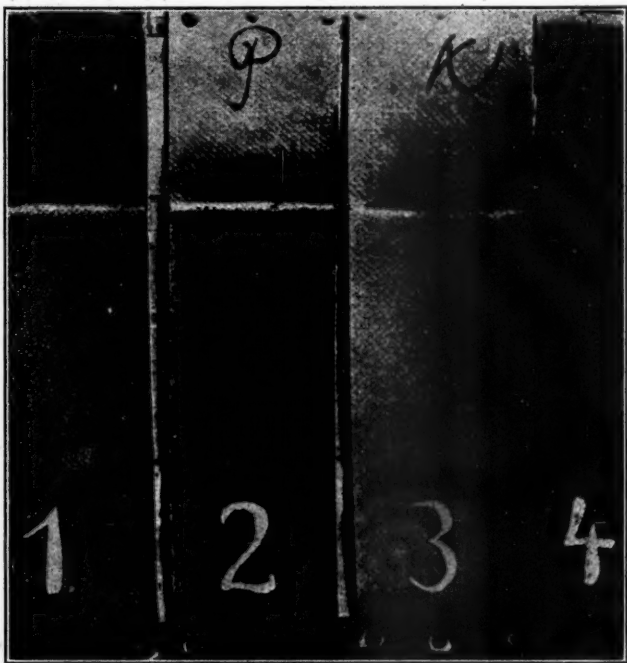


Figure 3—After 8 Weeks in Sunlight

Scale 1:2.5.

distance of 30 cm. from a Jänicke-mercury lamp at about 50° to 55° C. The results are shown in Figs. 8 and 9. It is particularly surprising that the boat material in which atmospheric cracks resulted in the shortest time showed the greatest loss of weight. On the other hand, the material on which cracks were slowest in appearing showed the smallest loss of weight. This may also be an explanation of the above results. When there is an opportunity, a longer and more detailed study of the losses and gains in weight of boat materials upon aging is to be made.

Protection of Collapsible Boat Materials against Cracking

According to Wurm⁶ a serviceable collapsible boat material should show no cracks after eight days' exposure in the open in summer and after a correspondingly

longer time in winter. This may be regarded as the minimum requirement; nevertheless this weathering test seems to be very short. A four-weeks' test should be made, since the boat material should be durable in service for several years. Longer tests of about three months⁷ or even six months give more precise results. Only two samples of the experiments in Table I satisfied the eight-day minimum requirement of resistance to weathering, while after two weeks all four samples had cracked, though these samples were in part obtained from leading shipyards. On account of this latter fact, it is evident that the experiments above were not inadvertently carried out solely with material of inferior quality.

Since the formation of cracks in unstretched boat material occurs not only more rapidly in sunshine than in the shade, but also appears sooner in the warm sunny months than in the cooler seasons, sunlight must be of fundamental importance.

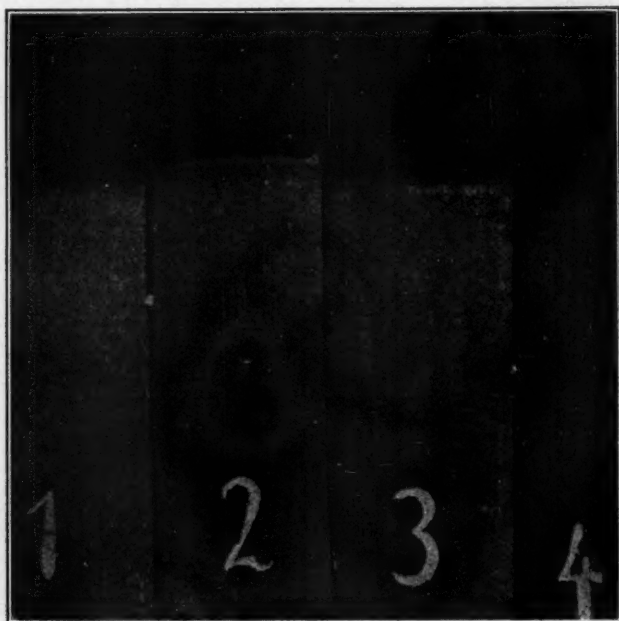


Figure 4—After 6 Months in Sunlight

Scale 1:2.5.

Moreover, according to Wurm (*loc. cit.*) weathering in winter requires a considerably longer time than in summer. Dawson⁸ is of the opinion that in order to preserve vulcanized rubber, actinic light must be kept away in addition to protection from oxygen.

The results in Table I show the necessity of a surface protection of boat coverings. Since, contrary to the experiments by van Rossem and Talen, in the case of collapsible boat materials no oxidized film of any practical value was formed spontaneously on the rubber as a self-protection, various methods of surface protection were studied.

Five types of material were tested: (1) waxes, (2) rubber products, (3) oil varnishes, (4) lacquers, and (5) combinations of coatings.

1. *Waxes*.—Under this designation all waxes and waxy substances, including paraffins, etc., are included. The use of paraffin, beeswax, ozocerite, ceresin, and wool grease in rubber mixtures is known.

In mixtures for collapsible boat material some paraffin⁹ is used, for example, and this migrates to the surface. The blooming of the wax on the surface of the boat material appears to me however to be in doubt, because in this way the pores would be free, and as a result the surface open to attack by oxygen would be considerably increased. Wax, paraffin, and similar substances produce inactive coatings which are especially protective against the action of *ozone*, and are of great importance in winter exposures. Paraffin protects the surface of boat material but only so long as the paraffin film is intact. It follows therefore that paints containing waxes must be continually replaced, since the wax once injured is easily rubbed off.

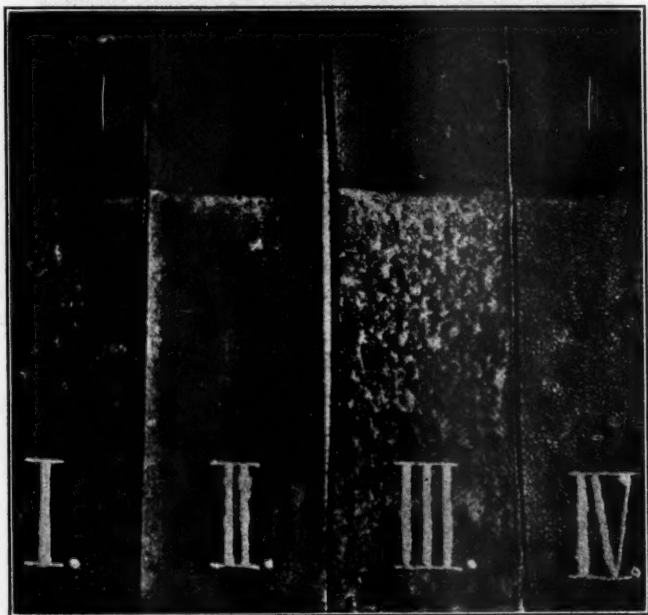


Figure 5—After 6 Months in Shade

Scale 1:2.5.

The use of wax and paraffin as waterproofing materials for fabrics has been known for a long time. Waterproof fabrics, for example, are impregnated with a solution of wax so that after evaporation of the solvent a thin layer remains. The paraffin coating on fabrics is, however, air- and waterproof only until the coating is cracked by folding the fabric, which makes it no longer water- and air-tight. These same phenomena apply to the treatment of collapsible boat materials with waxes, since the waxy substances are neither elastic nor plastic, but are brittle at the ordinary temperature in service, and therefore have a tendency to crack. Waxes are plastic only near their melting points, and the melting points are considerably higher than the temperatures that prevail in service.

The melting points can be lowered by admixing other substances, and the brittle-

ness can be diminished without producing elasticity. Moreover, it must be remembered that a mixture that is plastic at about 5-15° C. is already sticky above 25° C., which means that dirt and dust of all kinds will adhere to it. It is probably for

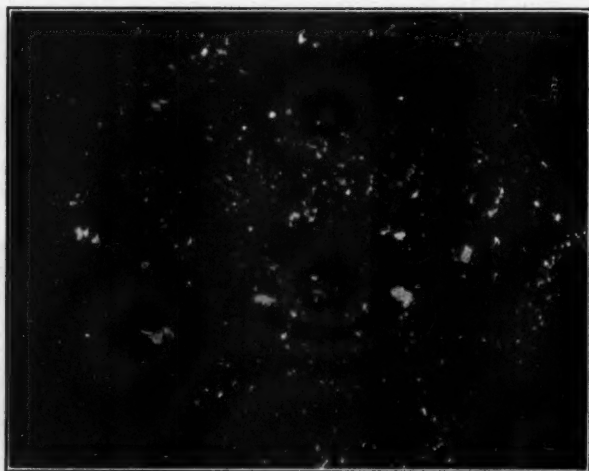


Figure 6—After 6 Months in Sunlight
(Figure 4, Sample 4 magnified 60 times)

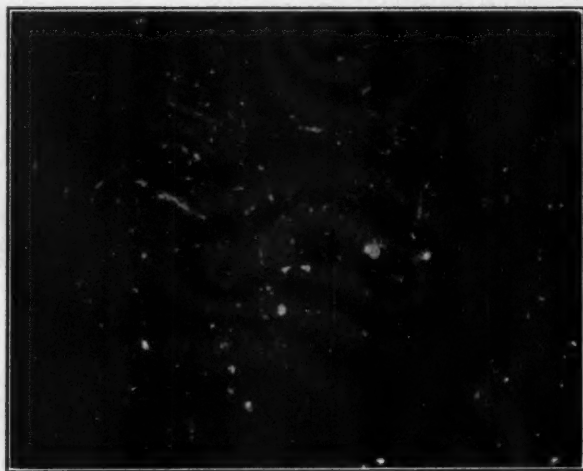


Figure 7—After 6 Months in Shade
(Figure 5, Sample 4 magnified 60 times)

this reason that most commercial wax preparations have a high melting point, under which conditions the danger of breaking at low temperatures (crack formation in the protective layer of waterproofing wax) is of course considered as the lesser evil.

Experiments on the resistance of waxes to weathering are shown in Table III. For this purpose the best material (No. 3 from the experiments in Table I) was used. One strip was left untreated for comparison. This collapsible boat ma-

TABLE II
MELTING POINTS OF WAXES AND WAXY SUBSTANCES¹⁰

(a) Paraffins	
Soft	40-42° C.
Medium	45-46°
Hard	50-52° and over
(b) Mineral waxes	
Ozocerite	58-72°
Ceresin	58-80°
(c) Vegetable waxes	
Canauba	83-91°
Flax wax	61-70°
Candelilla	67-70°
Montan	73-80°
(d) Animal waxes	
Spermacetti	42-45°
Wool grease	36-42°
Beeswax	63-64°
Chinese wax (insect wax)	80-83°
Shellac wax	72-75°

terial was coated twice with a waxy product made by a leading firm, and in addition to this a rubber product, and a combination of coatings was applied which were all the same color.

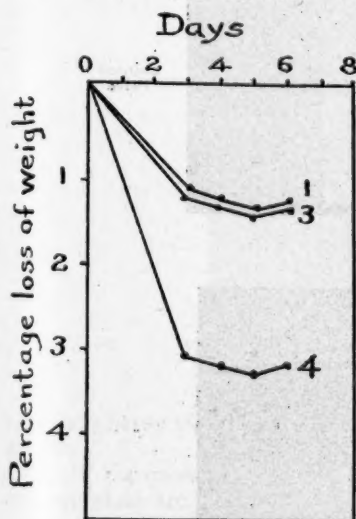


Figure 8—Effect of Heat

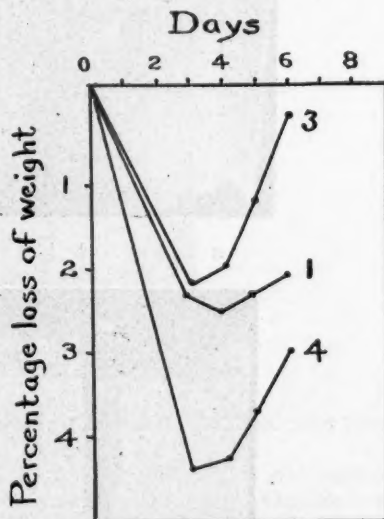


Figure 9—Effect of Ultra-Violet Radiation

After two weeks' exposure to sunlight the areas treated with wax had cracked like the untreated material. There did not appear to be any advantage in the treatment with wax. The rubber coating was still good after two weeks, but after three

months it was completely destroyed, while the combined coating was undamaged even after three months. For the most part the cracks in the wax were not perceptible, because there was little or no color contrast to distinguish them.

TABLE III
WEATHERING OF BOAT MATERIAL NO. 3 WITH VARIOUS PROTECTIVE AGENTS
Exposure toward the South Beginning in Summer

Protective Agent Material	No. of Coats	Two Weeks	Appearance after Exposure of Three Months
None	...	Cracks	Cracks
Wax	1	Cracks	Cracks
Wax	2	Cracks	Cracks
Rubber	1	Good	Strong crack formation and partly peeled off
Rubber	2	Good	Separate cracks (color wholly bleached)
Combination paint	1	Good	Good
Combination paint	2	Good	Good

2. *Rubber Solutions.*—The use of transparent or opaque rubber solutions is recommended because rubber solutions are used on the covering of collapsible boats. The tackiness of these solutions can be partly overcome¹¹ by the addition of ultra-accelerators by the aid of which self-vulcanizing solutions are formed, but this diminishes the stability of these solutions on standing. Upon storage, the

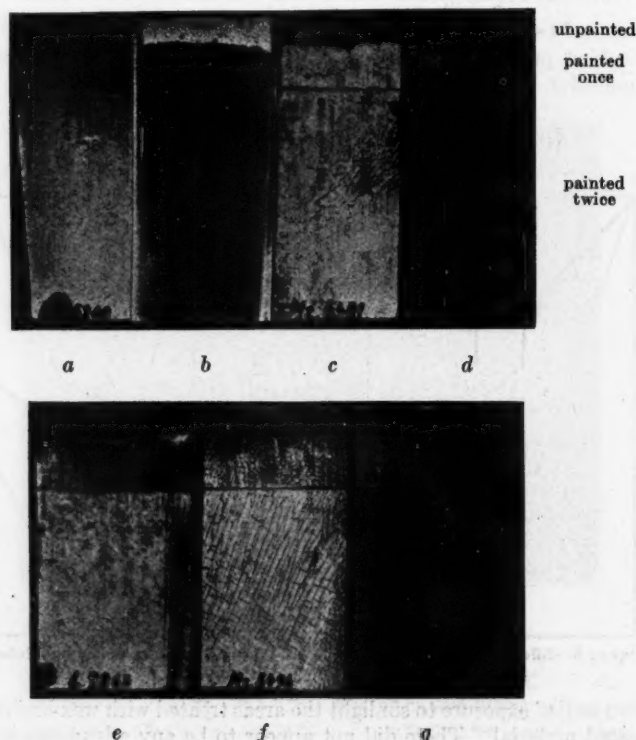


Figure 10—Combined Paints on Sample 4 after 5.5 Months' Weathering

solutions thicken to a jelly-like consistency and the application is made more difficult by the appearance of ropiness. In the trade there are also rubber solutions which must be mixed with the accelerator only just before their use, which is a somewhat bothersome process. The adhering power of so-called self-vulcanizing rubber solutions does not fully meet the claims made for them. Moreover coatings made from rubber solutions, because of their rubber content, undergo the same atmospheric deterioration as the collapsible boat material itself.

In the experiment in Table III, the prepared rubber product belonging to this boat material was applied to the best material (No. 3 in experiment in Table I). As is evident from Table III, the resistance to weathering of the rubber product was



h

i

k



l

m

n

Figure 11—Combined Paints on Sample 4 after 5.5 Months' Weathering

essentially better than that of the waxes; still the rubber was destroyed after three months.

3. *Oil Varnishes.*—Oil colors, oil varnishes, and oil varnish colors give lustrous coatings which are extremely resistant to the weather. On most collapsible boat materials, however, it is not possible to use them, since they do not dry because of the accelerator, antioxidant, waxes, and other substances in the rubber mixtures. Only on old, badly weathered boat material is a normal drying obtained, on account of the decomposition of the substances that retard drying. Since the elasticity of the oil film is less than that of the boat material, coatings with an oil base, especially old ones, have a strong tendency to form cracks upon stretching, stressing, or com-

pressing the film. Weathering tests of oil films on boat materials give apparently good results, in spite of their great brittleness. However, because of differences in the elasticity between the film and the rubber substance, there is a great tendency to crack upon compression or after longer aging.

4. *Cellulose Ester Lacquers*.—Cellulose ester lacquers have the advantage of an extremely fast rate of drying. On account of their resistance to weathering and their elasticity, cellulose nitrate lacquers have given good protection to rubberized coverings. The opposite is the case with boat materials because the power of adhesion is too slight on account of their wax content, so that the films peel off in large pieces.

Judged by the experiments on the four types of coatings, the requisites for serviceable paints and protective agents for collapsible boat materials are the following:

- (a) Drying capacity: on both old and new collapsible boat material.
- (b) Adhering power: on both old and new collapsible boat material.
- (c) Elasticity: at least the equivalent of the elasticity of collapsible boat material, with no cracking upon compression of the film and no greater loss of elasticity in the paint than in the boat material.
- (d) Resistance to weathering. No formation of cracks. The decrease in elasticity should not be greater than that of the collapsible boat material.
- (e) Protective action against sunlight. (It is still doubtful whether the cause of the destruction of rubber is to be attributed to invisible radiation, visible radiation, or to heat radiation.)
- (f) Stability of the unused coating during storage.
- (g) Ease of application.

These requisites have heretofore been fulfilled by no paint of the four groups. It is, however, possible to meet them by the proper choice and combination of suitable binding agents.

5. *Combination Coatings*.—Because of the great number of possibilities, the individual combinations lead to the most varied results. Figures 10 and 11 are representative of a large number of experiments and show the condition of different combinations of paints after five and one-half months' exposure to the weather (winter and summer). For these experiments the poorest product (No. 4 from experiments in Table I) was used, in order to obtain, by possible premature cracking of the boat material, the severest possible test of the paint. About one-tenth of the surface was unpainted, about two-tenths were painted once, and the remaining seven-tenths were painted twice. The samples were exposed to the weather toward the south, at an inclination of 45°.

Figures 10 and 11 show the most varied forms of destruction. Moreover, combinations *h*, *l*, and *m* fulfill the requisites specified above in that samples painted with these substances were intact after five and one-half months' weathering. By carefully peeling off varnishes *h*, *l*, and *m*, it was found that the collapsible boat material beneath was completely unchanged after five and one-half months, without any crack formation, although the same material (see Table I) without paint was completely cracked at the end of only 1 week. The films of paint after five and one-half months' weathering still showed a satisfactory elasticity. Accordingly, in this way the poor resistance to weathering of collapsible boat materials can be overcome by the immediate painting of the new material.

Summary

It was proved that in collapsible boat material, in contrast to pure rubber mixtures:

1. Cracks occur without stretching, and
2. Cracking takes place sooner in sunlight than in the shade.

Various possible ways are discussed for painting collapsible boat materials to protect them from cracking. The requisites for a serviceable paint are summarized. Waxes, rubber products, oil varnishes, and cellulose nitrate lacquers appear to be unsuitable because of various faults. Only combinations of paints of suitable composition meet these requirements. The poor resistance to weathering of collapsible boat materials can be overcome by immediately painting the new material.

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The Influence of Temperature on the Evolution of Hydrogen Sulfide from Vulcanized Rubber

A. D. Cummings

I. Introduction

This paper presents the results of measurements of the evolution of hydrogen sulfide from rubber-sulfur compounds heated at various temperatures. Determination of the amount of hydrogen sulfide produced under different conditions was used to measure the degree of decomposition of the rubber. Two types of experiments were carried out: (1) Samples of vulcanized rubber containing 8 to 32 per cent sulfur were heated for 8-hour intervals at 13 temperatures between 105° and 265° C., and (2) samples having sulfur contents of 4, 10, 18, and 32 per cent were maintained for about 200 hours at constant temperature, one set of specimens at 136° and another group at 220° C.

These measurements of deterioration were undertaken in connection with an investigation on the electrical properties of vulcanized rubber at relatively high temperatures. During these experiments, samples of rubber-sulfur compounds had been subjected to a wide range of temperatures. Time of exposure to each temperature had been about eight hours. The purpose of the present work was to determine when the sulfur content of a specimen had changed sufficiently to affect its dielectric constant and power factor by a measurable amount. In order to approximate the conditions under which the electrical tests were made, it was necessary to determine the amount of decomposition when rubber vulcanized with 8 to 32 per cent sulfur was heated for successive intervals of eight hours each at temperatures changed in unequal steps from 105° to 265° C. To make this information more complete and to obtain additional data which could be compared with previous investigations, the work was extended to include determinations of the loss of hydrogen sulfide from vulcanized rubber heated for a long time at constant temperature. The electrical properties of the whole series of rubber-sulfur compounds is the subject of a separate investigation at this bureau, and will be reported in another paper.

Many investigators have shown that hydrogen sulfide is associated with the vulcanization of rubber and with its subsequent deterioration during aging. Stevens and Stevens have noted the evolution of hydrogen sulfide during the vulcanization of ebonite at temperatures above 70° C. Webster, Fry, and Porritt have shown that ebonite evolves hydrogen sulfide at ordinary temperatures as well as when heated and have measured the rate of decomposition at several temperatures. Wolesensky has found that both soft and hard rubber lose hydrogen sulfide at all temperatures above 25° C. For more details of previous investigations on this problem during the last few years, the reader is referred to the papers by the authors mentioned.¹ A review of the literature up to 1929 is given in the paper by Wolesensky.

The results described in this paper represent a single set of measurements of the evolution of hydrogen sulfide when compounds of purified rubber and sulfur were heated under different conditions of time and temperature. Possible effects or variations which might be encountered with rubber samples made at different times

or prepared in different forms for exposure to the heat, or with other changes in experimental conditions were not investigated. The results show the loss of hydrogen sulfide when rubber-sulfur compounds representative of the whole series from soft to hard rubber were heated step by step from 105° to 265° C., and also when heated for 200 hours at 136° and at 220° C.

II. Preparation of Specimens

The rubber specimens were prepared from protein-free rubber hydrocarbon and sulfur. The rubber hydrocarbon was obtained from latex by digestion with hot water and extraction with water and alcohol, in accordance with the method described by McPherson,² which gives a purified material containing about 99.5 per cent hydrocarbon. A master batch of rubber and sulfur was made and portions of this were blended with fresh rubber hydrocarbon to give any sulfur content desired. The specimens were prepared by pressing samples of these rubber-sulfur mixtures

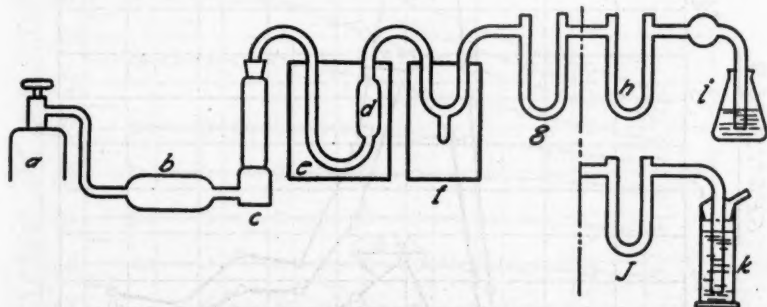


Figure 1—Apparatus Used for Measurement of Decomposition of Vulcanized Rubber

a, cylinder of commercial hydrogen to provide an inert atmosphere and sweep out products evolved while the rubber is heated.

b, concentrated alkaline pyrogallol solution on glass wool to absorb traces of oxygen.

c, tower containing calcium chloride and magnesium perchlorate to dry the gas stream.

d, glass tube containing the rubber sample cut into strips.

e, oil bath, electrically heated and thermostatically controlled.

f, trap in ice-salt freezing mixture to collect any volatile liquids.

g, U tube containing magnesium perchlorate to absorb moisture given off from the rubber.

h, U tube containing saturated potassium hydroxide solution on glass wool to absorb hydrogen sulfide, protected at each end by drying agent to prevent loss of moisture from the tube.

i, protective drying tube and bubble counter.

NOTE.—In some cases lead acetate solution was used as an absorber for hydrogen sulfide. This is indicated by the gas-washing bottle, k, preceded by the drying tube, j, to prevent back diffusion of moisture into the weighed drying tube, g.

between thin aluminum plates separated by a spacer 1.25 mm. in thickness. The specimens were then placed in an autoclave and vulcanized for 40 hours at 141° C. under pressure of carbon dioxide. The long period of vulcanization resulted in a product which contained practically no free sulfur in the soft and medium hard rubber ranges. In the case of pure hard rubber, analyses on different samples of stock containing 32 per cent sulfur showed from 0.5 to 0.8 per cent free sulfur. In the present experiments, the 32 per cent sample was the only one to show a deposit of sublimed sulfur.

III. Apparatus and Procedure for Determining the Hydrogen Sulfide Dissolved

The essential features of the apparatus were a supply of inert gas, a tube to hold the rubber sample, a constant temperature bath, and an absorber for the hydrogen sulfide. The individual parts of the apparatus are indicated and described in Fig. 1.

The general method chosen for measuring the deterioration of vulcanized rubber

when heated was determination of the amount of hydrogen sulfide evolved. This determination was carried out in two ways: (1) the hydrogen sulfide was absorbed in lead acetate solution and the lead sulfide collected and weighed, and (2) the hydrogen sulfide was absorbed by saturated potassium hydroxide solution contained in a tube which could be weighed directly. Both methods were equally satisfactory under appropriate conditions. Absorption in lead acetate is preferable when a very small amount of hydrogen sulfide is to be measured, but when much lead sulfide is

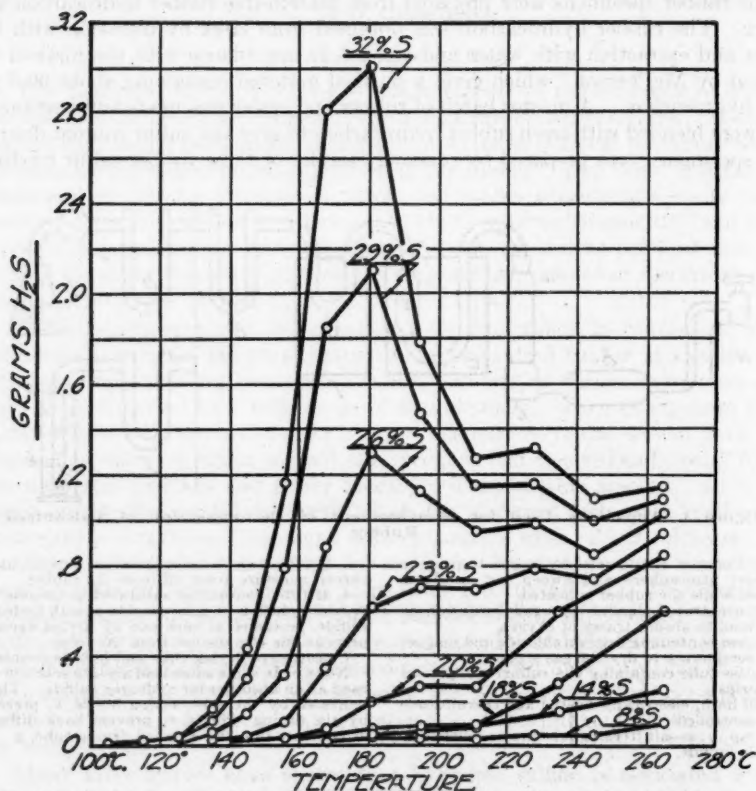


Figure 2—Evolution of Hydrogen Sulfide from Vulcanized Rubber during Step-by-Step Heating

Grams of hydrogen sulfide liberated from 100 g. vulcanized rubber heated for eight hours at each temperature indicated. Every sample was started at 105° and the same sample was carried through to 265°.

formed this method becomes exceedingly time-consuming on account of slow filtration.

1. *Measurement of the Evolution of Hydrogen Sulfide during Step-by-Step Heating.*—The decomposition in this part of the work was carried out with a simplified apparatus consisting of gas supply, sample tube and heater, trap, and hydrogen sulfide absorber. In order to duplicate more nearly the conditions during the electrical test when the inert gas was not purified, the purifying train was omitted. The drying tube, *g*, was not used because it was not intended to account for all products formed. Only sections *a*, *d*, *e*, *f*, and *k* of the apparatus were employed.

The tubes containing 5-gram samples of rubber in strips cut from the specimens previously described were placed in the oil bath and the stream of hydrogen³ started. The bath was heated from room temperature up to 105° C. where it was held for eight hours. The absorber containing lead acetate solution was then changed, provided any precipitated lead sulfide was visible, and the temperature was raised to 115°. The lead sulfide formed was collected by filtration through a Gooch crucible, washed, dried, and weighed. This procedure was repeated step by

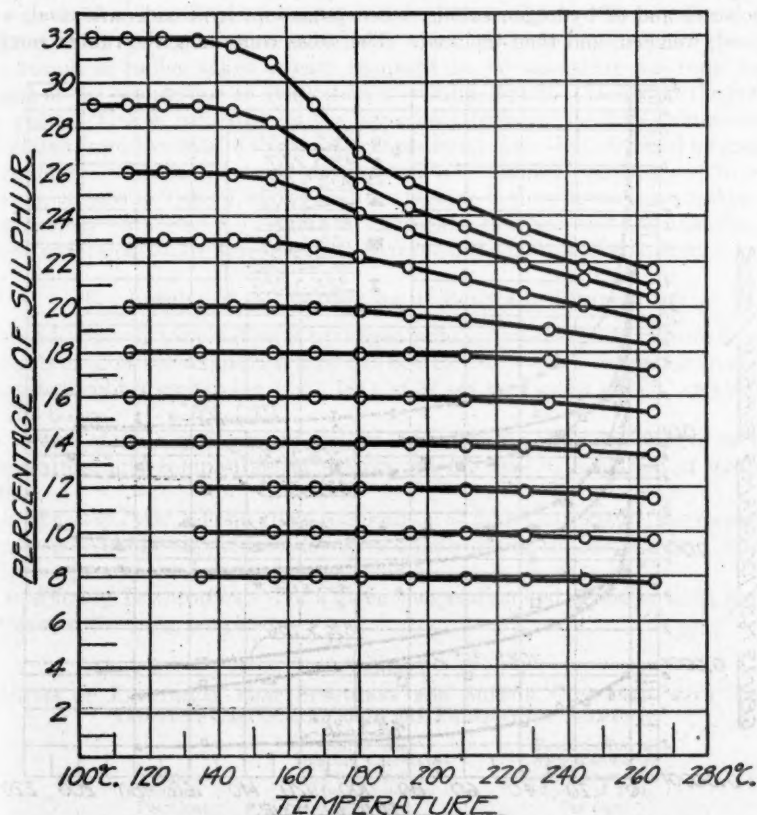


Figure 3—Change in Sulfur Content of Vulcanized Rubber during Step-by-Step Heating

Samples were heated for eight hours at each temperature indicated by the various points. Every sample was started at 105° and the same sample was carried through to 265°.

step every eight hours at 13 temperatures between 105° and 265°, with samples containing from 8 to 32 per cent sulfur. All samples were heated for eight hours at each temperature before being raised to the next higher temperature. It was already known that the electrical properties of rubber containing less than 8 per cent sulfur were not changed a significant amount by loss of sulfur when heated under these conditions, consequently the experiments were begun with the 8 per cent compound. Temperatures below 100° did not cause a change in sulfur content sufficient to be detected in the electrical measurements on a specimen containing the

maximum amount, 32 per cent, of sulfur, therefore 105° was selected as the initial temperature.

2. *Measurement of the Evolution of Hydrogen Sulfide at Constant Temperature.*—The apparatus was used complete as described for this part of the investigation, and both methods for the absorption of the hydrogen sulfide were employed. The specimen tubes containing 20 to 50 g. of rubber were set up at room temperature outside the oil bath. While the bath was being heated to the temperature desired, the apparatus was swept with hydrogen to displace air. The tubes for absorption of moisture and of hydrogen sulfide, when potassium hydroxide was used, were removed, weighed, and then replaced. The tubes containing the rubber samples

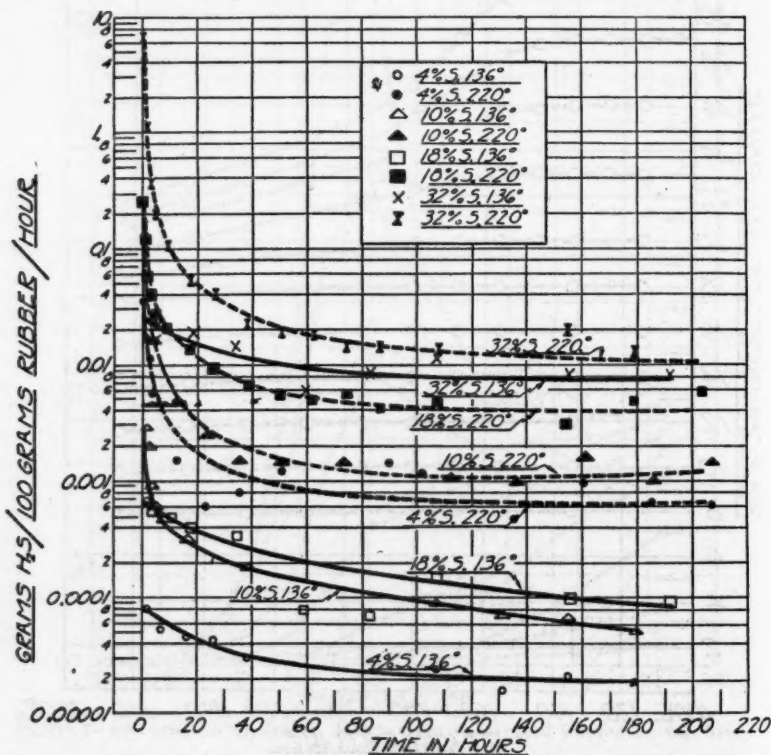


Figure 4—Rate of Evolution of Hydrogen Sulfide from Vulcanized Rubber Heated at 136° and 220° C., Plotted on a Semilogarithmic Scale

were next immersed in the hot oil, and the hydrogen stream was adjusted to about one bubble per second. The hydrogen sulfide was measured at intervals by weighing the U-tube absorbers directly or by determining the amount of lead sulfide formed. The amount of moisture and volatile oils was determined only at the end of the experiment. This served to account for the entire loss in weight of the samples. The loss of hydrogen sulfide was determined for four rubber compounds containing 4, 10, 18, and 32 per cent sulfur when samples were heated for about 200 hours at 136° C., and also when other samples were heated at 220° C. for the same length of time. The temperature of the oil bath was held within $\pm 1^\circ$ at the former temperature and $\pm 3^\circ$ at the latter.

IV. Results of Decomposition during Step-By-Step Heating

The evolution of hydrogen sulfide from vulcanized rubber containing 8 to 32 per cent sulfur when heated in the 8-hour stepwise manner increases with rising temperature, with the exception that the loss from the compounds containing the higher percentages of sulfur passes through a maximum. In view of the large change in sulfur content during heat, this is not surprising. The amount of hydrogen sulfide evolved in an 8-hour interval at each temperature is shown in Fig. 2.

The change in sulfur content calculated from the loss of sulfur as hydrogen sulfide between 105° and each higher temperature is given in Fig. 3. These values for the sulfur content are not identical with those which would be determined by analysis of a sample of rubber taken at each temperature, because there was some loss in weight of the sample due to distillation of volatile liquids. However, the error is not great. This is indicated by the agreement between the final sulfur content calculated from the data of the present experiments and that obtained by analysis of samples used in the electrical measurements mentioned previously. This comparison, printed in Table I, shows that the heating in the present investigation had satisfactorily paralleled the conditions during the electrical test and that the procedure and calculations were adequate to furnish the information desired.

V. Results of Decomposition at Constant Temperature

In addition to determination of hydrogen sulfide, measurements were made of the amounts of other decomposition products and moisture which resulted from heating vulcanized rubber containing 4, 10, 18, and 32 per cent sulfur at 136° and 220° C. for 200 hours.

1. *Rate of Loss of Hydrogen Sulfide.*—The results show the effects of time, temperature, and composition of samples on the rate of evolution of hydrogen sulfide.

(a) *Effect of Time.*—For a given composition at each temperature, the rate of loss of hydrogen sulfide, high at first, decreases rapidly during the first few days' heating, but subsequently the decrease becomes slow.

(b) *Effect of Temperature.*—For a given composition and period of time, the rate increases with rising temperature.

TABLE I
ANALYSIS OF ELECTRICAL TEST SPECIMENS FOR SULFUR COMPARED WITH SULFUR CONTENT CALCULATED FROM THE PRESENT EXPERIMENTS

Original Sulfur, Per Cent	Sulfur after Heating Calculated from Present Measurements, Per Cent	Total Sulfur in Specimens after High Temperature Electrical Test, Per Cent
32	21.6	22.0
29	20.9	21.5
26	20.4	20.5
23	19.3	19.6
20	18.3	18.1
18	17.0	16.8
16	15.4	15.2
14	13.4	13.4
12	11.4	11.1
10	9.6	9.5
8	7.7	7.8

(c) *Effect of Composition of Samples.*—For a given temperature at equal times, the rate increases as the sulfur content of the rubber becomes greater, with one

exception, namely, that there is a noticeable similarity between the 10 and 18 per cent compounds in loss of hydrogen sulfide at 136°. This observation was satisfactorily repeated.

The rate of evolution of hydrogen sulfide from the samples investigated is shown in Fig. 4. These curves are started at the point of maximum evolution, an initial increase in rate being disregarded because it must be due only to the heating up of the sample and the approach to a quasi-steady state throughout the apparatus. The percentage of the original weight lost as hydrogen sulfide plotted against the time is given in Fig. 5.

2. *Other Decomposition Products and Moisture.*—Along with the hydrogen

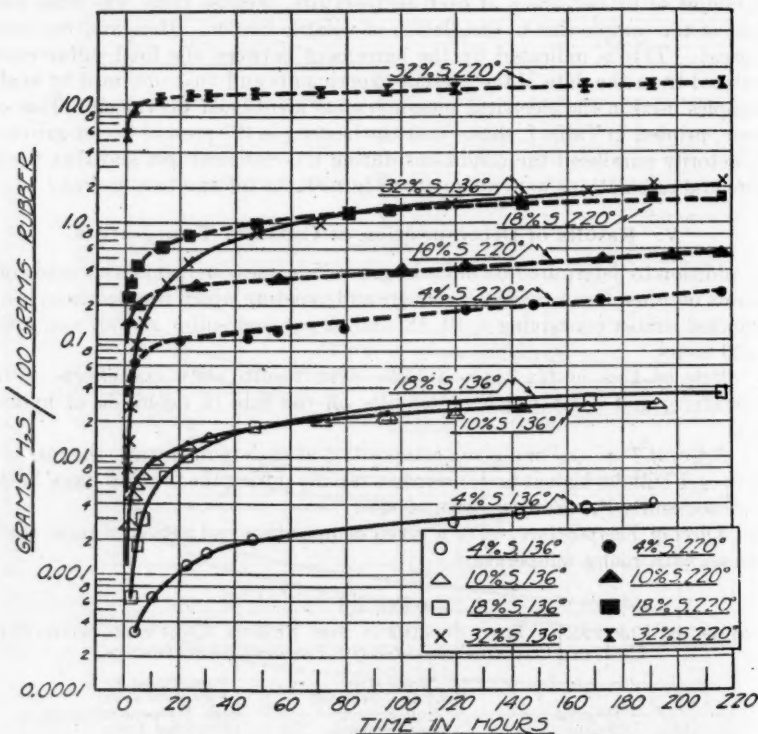


Figure 5—Percentage Loss of Hydrogen Sulfide at 136° and 220° C., Plotted on a Semilogarithmic Scale

sulfide, volatile oils having slight terpene-like odors were formed. At 220°, these oils made up 10 to 40 per cent of the total loss in weight of the samples during 200 hours' heating. There was also a trace of some compound having a faint onion-like odor which was never condensed or absorbed by potassium hydroxide or lead acetate. No attempt was made to identify this or any of the other organic products. Some moisture⁴ was evolved from the rubber and was measured at the end of each group of experiments in order to be able to account for the entire loss in weight of the samples. The percentage of the original weight obtained in the products from a typical experiment with a 32 per cent compound at 136° is given in Table II, which shows that the total loss was satisfactorily accounted for.

VI. Characteristics of the Rubber after Heating

The specimens all changed materially in physical properties during the exposure to heat. Compounds which had initially contained up to 26 per cent sulfur became translucent and showed a reddish color when samples 1 mm. in thickness were examined in sunlight, whereas all above 12 per cent of sulfur were originally opaque. At the end of the heating, the intermediate and hard rubbers were brittle at room

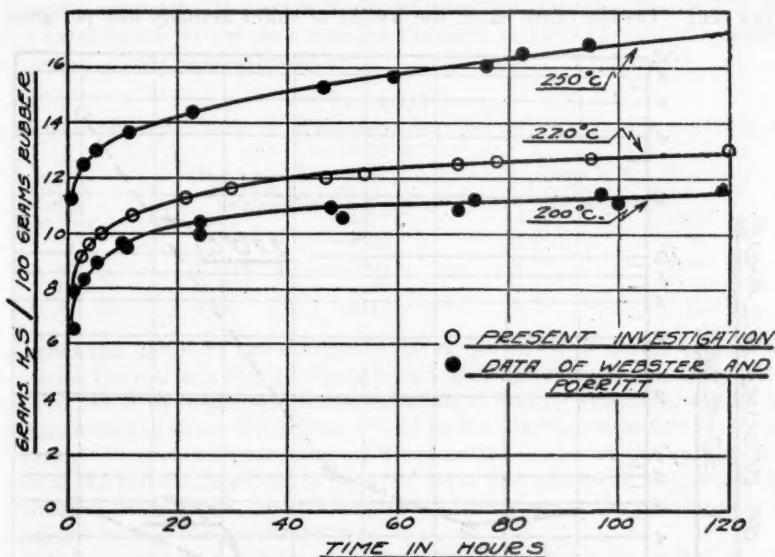


Figure 6—Comparison between Present Data and Those of Webster and Porritt. (See Footnote 1, p. 55)

Loss of hydrogen sulfide from hard rubber at 200°, 220°, and 250° C.

temperature, but became flexible and tacky when warmed. A similar change in properties, less in degree, was evident in the samples of soft rubber. The conversion of vulcanized rubber into thermoplastic materials has been noted by Kemp,⁸ who heated rubber mixed with 8 to 16 per cent sulfur to 200° to 280° C., and the manufacture of such products from raw rubber is now a commercial process.

TABLE II

PERCENTAGE OF ORIGINAL SAMPLE ACCOUNTED FOR AFTER A 32 PER CENT COMPOUND WAS HEATED 200 HOURS AT 136° C.

	Per Cent
Residual rubber.....	95.55
Oils.....	0.01
Sulfur.....	0.02
Moisture.....	0.18
Hydrogen sulfide.....	2.17
Total.....	97.93

VII. Discussion

The course followed by the loss of hydrogen sulfide when vulcanized rubber is heated is well established and agrees with the results of previous investigations so far as can be told from consideration of the data taken under different conditions.

The curve for evolution of hydrogen sulfide from the 32 per cent compound at 220° lies between similar curves published by Webster and Porritt⁶ for ebonite heated at 200° and 250° C. This comparison is shown in Fig. 6.

Calculation of the ratio of sulfur lost at the end of 190 hours to the initial sulfur content shows that the percentage of the original sulfur lost at 136° is greater for the compound containing 10 per cent sulfur than for that containing 18 per cent, and at 220° is greater for the compound containing 4 per cent sulfur than for that having 10 per cent. On the other hand, the weight of sulfur actually lost per gram of

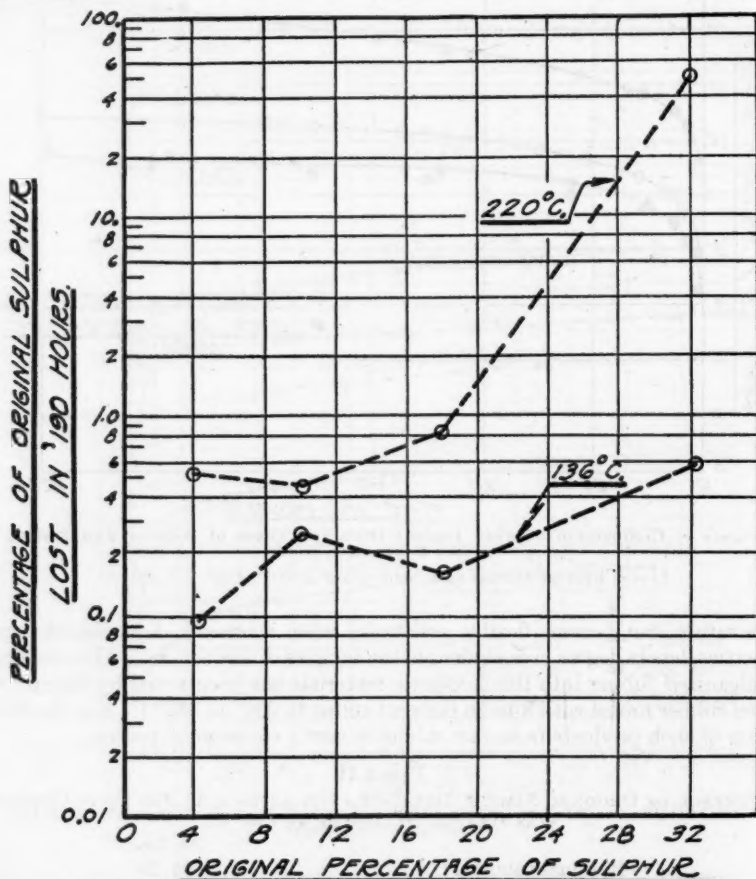


Figure 7—Percentage of Original Sulfur Lost in 190 Hours at 136° and 220° C., Plotted on a Semilogarithmic Scale as a Function of Initial Sulfur Content

rubber compound was nearly equal for the 10 and 18 per cent compounds at 136° and was less for the 4 per cent sample than for that containing 10 per cent sulfur at 220°. These calculations are given in Table III and the proportionate loss of sulfur is plotted in Fig. 7. The similarity in rate and in total percentage of loss at 136° for the samples containing 10 and 18 per cent sulfur led to a repetition of this experiment over the first 80 hours using other specimens containing the same percentages of sulfur. This determination checked the original observations satisfactorily. Also, an inspection of the data from the earlier experiments showed a

distinct similarity in rate of evolution from compounds containing 10 to 18 per cent sulfur at the lower end of the temperature range. These observations can be interpreted as indicating that there may be a range of compositions, varying with the temperature, where rates of decomposition are similar, and where the proportionate loss of sulfur may grow less while the original sulfur content of the specimens increases. There may be a fairly sharp break at the end of this range, above which the loss of hydrogen sulfide may become much more rapid and follow the course expected for the order of ascending sulfur content. The data of the present experiments do not show whether the cases at hand are part of a general phenomenon or only isolated instances.

TABLE III
COMPARISON BETWEEN LOSS OF HYDROGEN SULFIDE AND PROPORTIONATE LOSS OF SULFUR

Original Sulfur, Per Cent	H ₂ S Lost at End of 190 Hours as Per Cent of Original Compound		Sulfur Lost in 190 Hours as Per Cent of Original Sulfur	
	136°	220°	136°	220°
4	0.004	0.23	0.094	5.29
10	0.029	0.51	0.26	4.58
18	0.033	1.56	0.17	8.15
32	1.96	13.92	5.77	40.93

The chemical nature of the changes in the rubber molecule during thermal decomposition has not been thoroughly explained, although change in unsaturation as a result of loss of hydrogen sulfide and the effect of heat on vulcanized rubber has been commented upon by Winkelmann,⁷ and by the other investigators previously mentioned.⁸ A few determinations of unsaturation made on the rubber after heating in the present experiments have not given any additional insight into the mechanism of the chemical changes involved. This phase of the problem may be investigated further at some future time.

Since this manuscript was prepared, a paper on the pyrolysis products of ebonite by Midgley, Henne, and Shepard has been published.⁹

The author wishes to express his thanks to A. H. Scott for assistance with some of the measurements reported in this paper.

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- ¹ Edward Wolessensky, *B. S. Jour. Research*, **4**, 501 (1930); *Rubber Chem. Tech.*, **3**, 386 (1930). J. D. Fry and B. D. Porritt, *India Rubber J.*, **78**, 307 (1929). D. M. Webster and B. D. Porritt, *Ibid.*, **79**, 239 (1930); *Rubber Chem. Tech.*, **3**, 618 (1930). H. P. Stevens and W. H. Stevens, *J. Soc. Chem. Ind.*, **50**, 397T (1931).
- ² A. T. McPherson, "A Method for the Purification of Rubber and Properties of the Purified Rubber," *B. S. Jour. Research*, **8** (RP449), 751 (1932).
- ³ No significant error was introduced by reaction of the hydrogen with any small amount of freed sulfur in the rubber. The rate of reaction of hydrogen with sulfur is relatively slow at the highest temperature used in the present experiments. (See J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1930, vol. 10, pp. 117 ff.) Furthermore, an experiment in which steam was used as the inert gas gave substantially the same rate of evolution of hydrogen sulfide as was obtained with hydrogen (unpublished work of A. T. McPherson).
- ⁴ The moisture may have been an impurity or may have come from the thermal decomposition of a small amount of oxidized material in the rubber. For a discussion of the products formed by oxidation of rubber, see A. R. Kemp, W. S. Bishop, and P. A. Lasselle, "Oxidation Studies of Rubber, Gutta-Percha, and Balata Hydrocarbons," *Ind. Eng. Chem.*, **23**, 1444 (1931).
- ⁵ A. R. Kemp, U. S. Patent 1,638,535, Aug. 9, 1927. For a general review of the field of thermoplastic products made from rubber, including patent references, the reader is directed to Harry L. Fisher, "Chemistry of Rubber," *Chem. Rev.*, **7**, No. 1, 94, 112-123 (March, 1930).
- ⁶ See footnote 1, 46.
- ⁷ H. A. Winkelmann, *Ind. Eng. Chem.*, **18**, 1163 (1926).
- ⁸ See footnote 1, 46, and footnote 5, 53.
- ⁹ T. Midgley, Jr., A. L. Henne, and A. F. Shepard, *J. Am. Chem. Soc.*, **54**, 2953 (1932).

Studies on the Thermochemistry of the Vulcanization of Rubber

VII. Heating Curves for the Vulcanization of the System: Raw Rubber-Sulfur (2)¹

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Introduction

A preliminary report of this experiment was presented at the 34th annual meeting of the Society of Chemical Industry of Japan. The present report deals with a further study and an improvement of the method.

Heating curves for the vulcanization of the system: raw rubber-sulfur have been studied by Williams and Beaver (*Ind. Eng. Chem.*, 15, 255), Perks (*J. Soc. Chem. Ind.*, 45, 142), and Toyabe (*J. Soc. Rubber Ind. Japan*, 4, 514 (1931)). Williams and Beaver reported the results obtained in finding the heating curves of

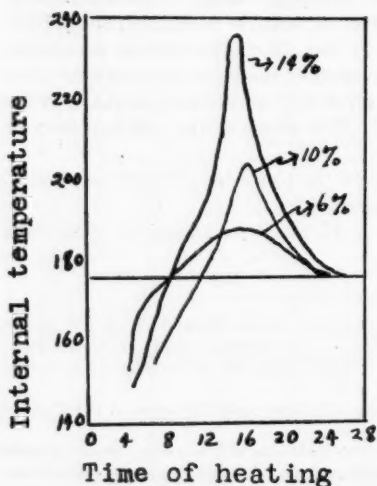


Fig. 1

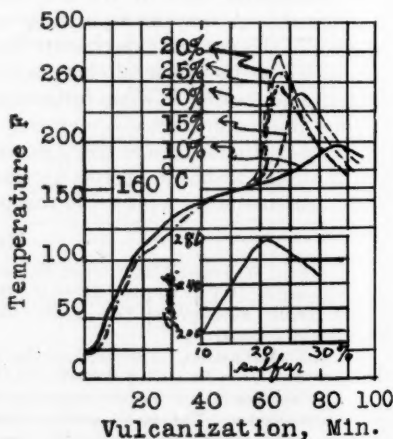


Fig. 2

three samples of rubber compounded with 6, 10, and 14 per cent of sulfur, and noted that the amount of heat evolved by the reaction was increased by an increased addition of sulfur (as shown) in Fig. 1. Perks studied the change in temperature, during vulcanization, of the interior of the samples, which were compounded with 10, 15, 20, 25, and 30 per cent of sulfur. The internal temperature of the samples increased with increase in the sulfur content up to 20 per cent, and it decreased when the sulfur content was above 20 per cent, as shown in Fig. 2. Such a phenomenon as a de-

¹ This paper was presented before the 54th annual meeting of the Chemical Society of Japan at the Kyoto Imperial University, May 4, 1932.

crease in the heat evolved when the sulfur content of the rubber is over 20 per cent is not explainable by any present knowledge of rubber chemistry. Toyabe studied the increase in internal temperature of samples compounded with 10, 20, and 32 parts of sulfur, respectively, per 68 parts of rubber. The result indicated that the time required to reach a maximum internal temperature is the same, regardless of difference in compounding, as shown in Fig. 3.

Experimental Procedure

Thermocouples made of copper constantan of 0.1 mm. diameter were connected with each other in such a way that one end was placed in an unvulcanized sample of a raw rubber-sulfur system (A) and the other in a sample of the same composition which had already passed through a vulcanization process and was thermally inactive (B). In order to obtain insulation between the thermocouples outside the sample, and to prevent sulfide formation between the thermocouple and sulfur in the sample, the wire was covered with cellophane. In our previous work on heating pure raw rubber, an acetone solution of cellulose acetate was coated over the

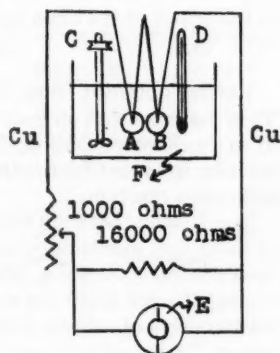
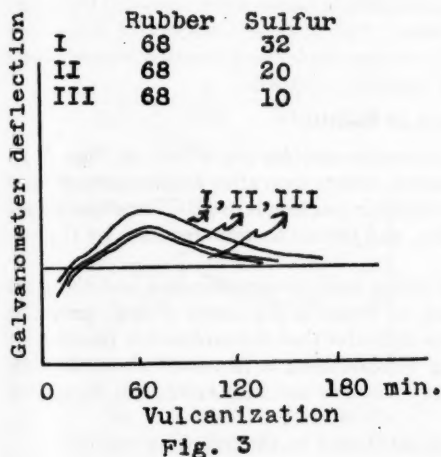


Fig. 4

wire, but this coating was useless in this experiment because of evolution of heat by the vulcanization reaction, which broke the coating. The ends of the thermocouples were placed in the center of the sample to be vulcanized (A) and in the thermally inactive sample (B). These were wrapped with doubled thin silk cloth and then with cellophane to prevent direct contact with the oil in the oil bath (F). The purpose of using such wrapping materials instead of metallic containers was to decrease the heat capacity of the vessel to as little as possible and to obtain an accurate measurement of the internal change of temperature without interference. The diameter of the unvulcanized (A) and vulcanized (B) samples was the same—15 mm. for samples of the first half, and 10 mm. for samples of the latter half of the experiment. The (Cambridge-made) Miller galvanometer used had a 107-ohm internal resistance. The circuit was made through a 1000-ohm resistance in series with a 1600-ohm shunt. The unit of reading was 1-mm. deflection, which was equivalent to a thermal change of 0.143°C . The connection is indicated in Fig. 4. The shunt was used to facilitate a quick reading of the deflection, but the effect is doubtful. The thermostat for heating the samples was made of an electrically

heated oil bath. The unvulcanized (A) and vulcanized (B) samples were placed at the center of the bath. The oil bath consisted of an agitator (C), a regulator, and a thermometer (D). When the temperature of the bath remained unchanged at 70° C., and the galvanometer reading was zero and remained constant for 10 minutes, the bath was heated, and the readings were made during the heating. The heating was stopped when the temperature of the bath became 160° C. and remained constant for more than 100 minutes. At the end of the experiment the circuit was disconnected, and it was noted that the galvanometer reading remained at zero. The readings were made every 30 seconds during the rapid vulcanization reaction, but when the reaction slowed down they were made at 1 or 5 minute intervals.

Samples

The materials used in this experiment were a standard smoked sheet and sulfur free from acid. Fifteen samples of 15-mm. diameter were made of 3, 5, 10, 15, 20, 25, 30, 35, 36, 38, 40, 45, 50, 60, and 70 parts of sulfur per 100 parts of raw rubber, and 7 samples of 10-mm. diameter were made of 5, 10, 20, 30, 40, 50, and 60 parts of sulfur per 100 parts of raw rubber.

These samples were calendered to approximately 1-mm. thickness, and the round discs were folded into a semi-circular form. Two of these semicircular forms were attached together to form a round disc, a thermocouple being inserted between them at the center of the discs and the entire unit was wrapped.

Discussion of Results

Results obtained from the 15-mm. diameter samples are shown in Figs. 5-19. These indicate that an endothermic reaction occurs soon after heating, which turns to an exothermic reaction after the endothermic reaction is over. The endothermic reaction is caused by the fusion of sulfur, and the exothermic reaction by the vulcanization reaction.

The relation between the amount of sulfur used in compounding and the point of maximum exothermic heat developed, as found in the curve of each sample, is shown in curve A of Fig. 20. The curve indicates that the exothermic reaction becomes stronger when the sulfur used in compounding is increased above 30 parts for 100 parts of rubber, but this tendency becomes less with more than 50 parts of sulfur.

The break in the exothermic curve is attributed to the following causes:

1. A substitution reaction besides an addition reaction in the double bonds of isoprene, when the vulcanization reaction raises the temperature above the limit of internal temperature.

2. An unbalanced heat evolution and loss of heat by conduction.

Should there be any substitution reaction, as in the first case, there should be an evolution of hydrogen sulfide. The evidence is that those samples compounded with more than 30 parts of sulfur left some gaseous pores. In the second case the extent of the rise in the internal temperature is lowered either by decreasing the speed of heating during vulcanization (a decrease in the quantities of heat evolved in unit time) or by decreasing the diameter of samples (an increase in the heat conductivity due to an increase of relative surface area). This is explained by the fact that the samples of 15-mm. diameter decreased in size, by raising of the internal

EXPLANATION OF FIGS. 5 TO 19 AND 21 TO 27

The left-hand column indicates the galvanometer deflection in centimeters, the right-hand the change in temperature in F. degrees, and the bottom line indicates the time of vulcanization in minutes.

In Figs. 15 to 19 R stands for rubber and S for sulfur.

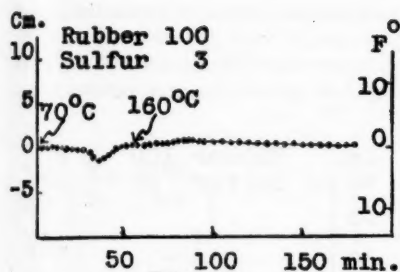


Fig. 5

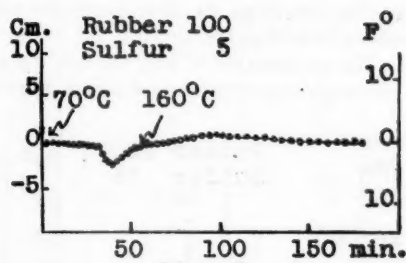


Fig. 6

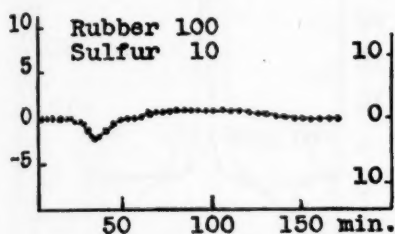


Fig. 7

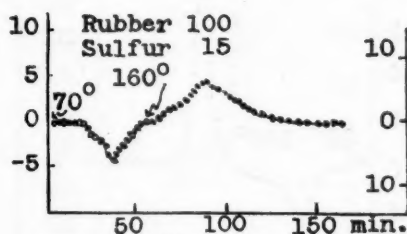


Fig. 8

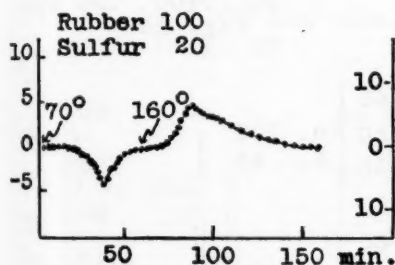


Fig. 9

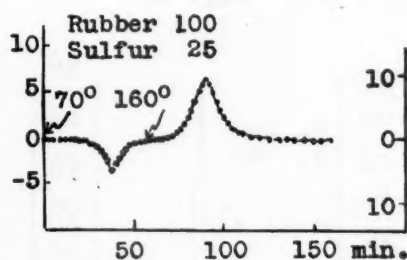


Fig. 10

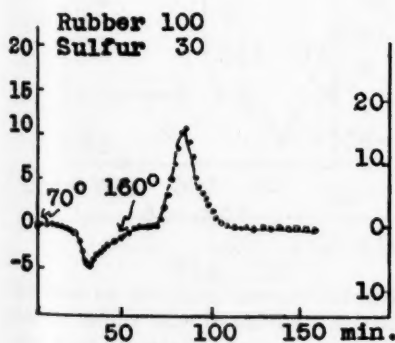


Fig. 11

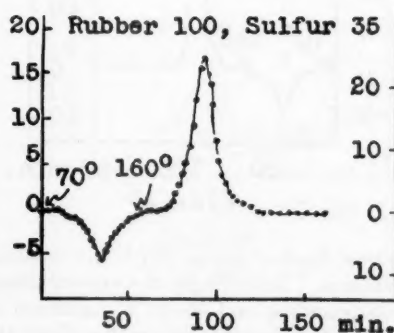


Fig. 12

temperature, to $\frac{2}{3}$ of the diameter, as shown in curve A (15 mm.) and B (10 mm.) in Fig. 20. Figs. 21-27 indicate the individual heating curves of vulcanization of curve B in Fig. 20.

The explanation of why the heating curves lower when the amounts of sulfur in compounding are increased above 50 parts is that 50 parts is the approximate theo-

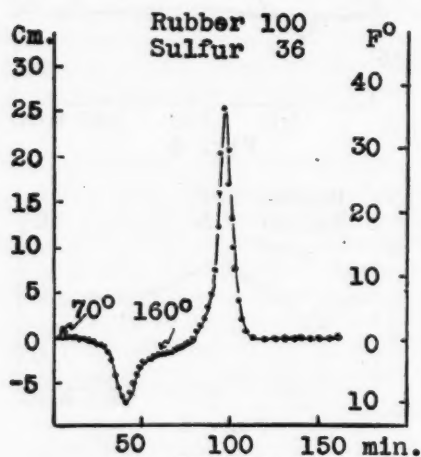


Fig. 13

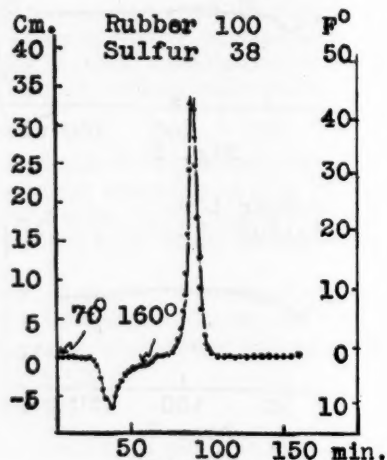


Fig. 14

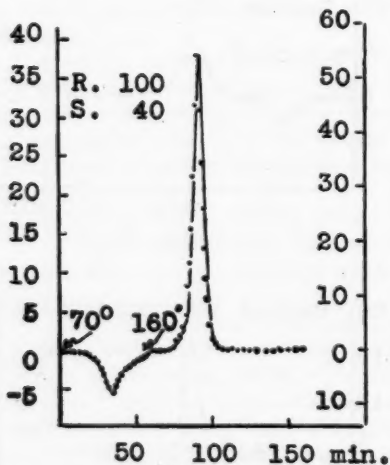


Fig. 15

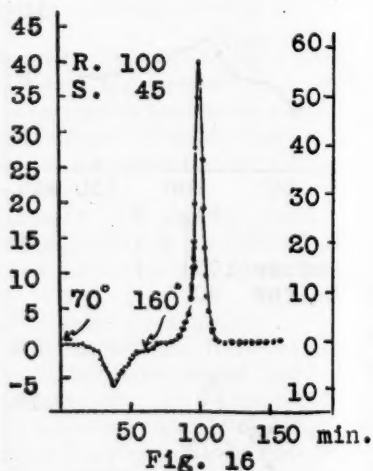
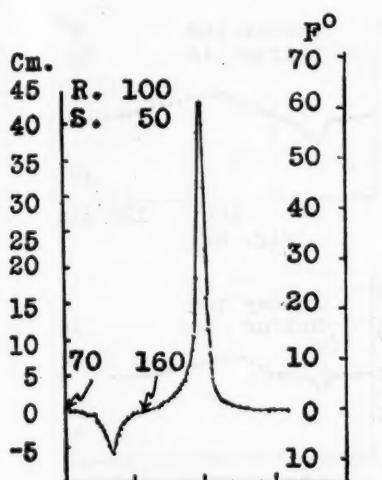


Fig. 16

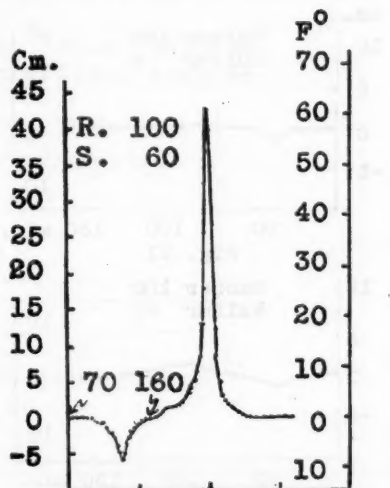
retical limit of sulfur which can combine with the isoprene group by an addition reaction. Accordingly the vulcanization reaction is saturated with sulfur in this compounding and shows a maximum exothermic reaction. Since the heat conductivity of sulfur is greater than that of rubber or vulcanized rubber, and the excess of sulfur dilutes the heat of reaction, the maximum heat evolution in the curves is thus lowered when the sample contains above 50 parts of sul-

fur. When the diameter of the samples was increased, there was a tendency to a sudden increase in the rate of the exothermic reaction in compounds of lower sulfur content, and the rate of increase of the internal temperature became



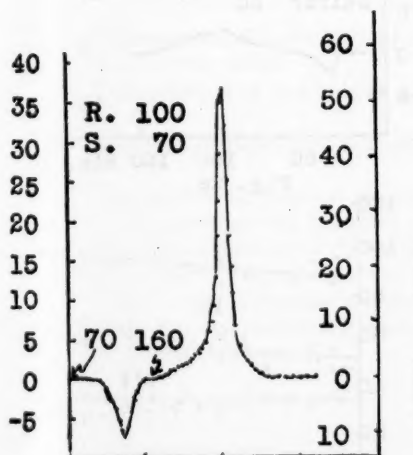
50 100 150 min.

Fig. 17



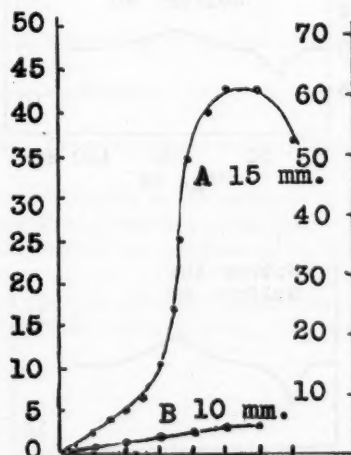
50 100 150 min.

Fig. 18



50 100 150 min.

Fig. 19



20 40 60 80

Sulfur

Fig. 20

still greater in such compounds. This was to be expected, and it conforms to the vulcanization of ebonite. The relation of time to the endothermic end points from the fusion of sulfur and the exothermic end point is shown in Fig. 28. Line I

indicates the required time from the first heating to the end of the exothermic vulcanization reaction. Line III indicates the time required from the first heating to the beginning of the exothermic vulcanization reaction, and that of II from the end

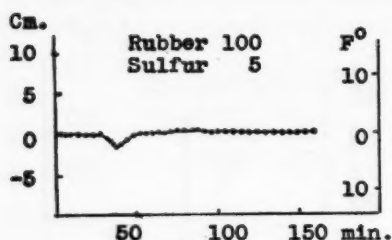


Fig. 21

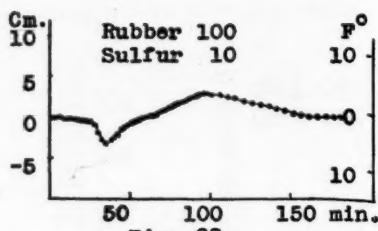


Fig. 22

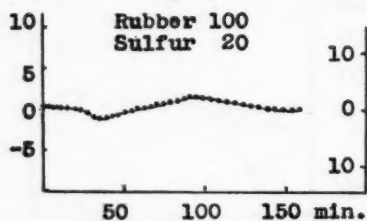


Fig. 23

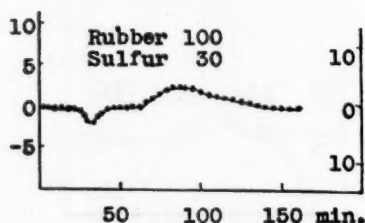


Fig. 24

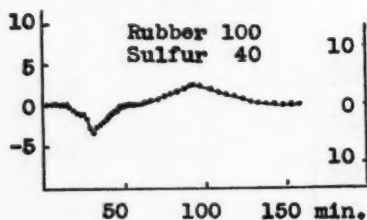


Fig. 25

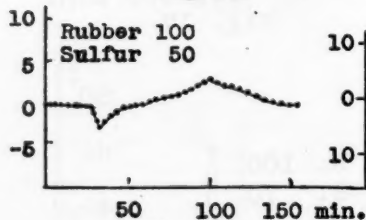


Fig. 26

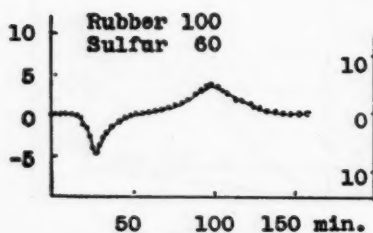


Fig. 27

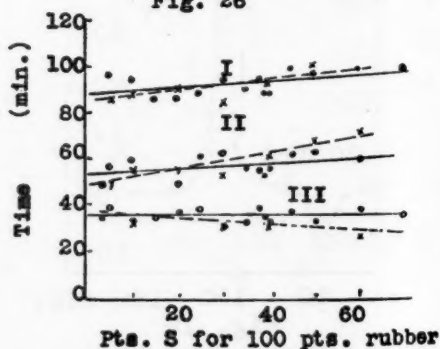
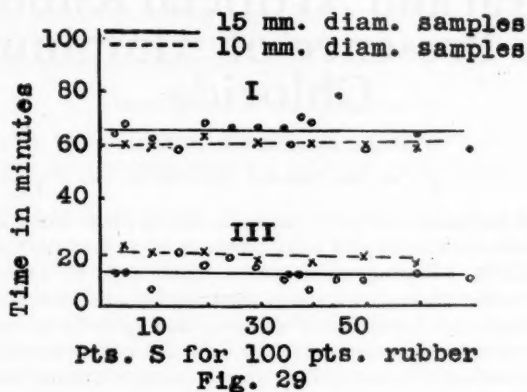


Fig. 28

of the fusion of sulfur to the end of the exothermic vulcanization reaction. Although the differences of these time relations were slight, there were tendencies to increase or decrease when different amounts of sulfur were used in the compounds.

Although such end points are generally discussed, they are without much meaning, and the studies of the points of starting of endothermic (III) or exothermic (I) reactions as shown in Fig. 29, are more important. This indicates that the time which shows the thermal effect is not influenced by the different amounts of sulfur



used in compounding; this conclusion, however, is meaningless unless the conditions of heating are identical in all cases. In our experiment, caution was taken to keep the samples in the thermostat at 70° C. for some time and the samples were heated under the same conditions.

Conclusions

1. Vulcanization of raw rubber by sulfur is preceded by an endothermic reaction from fusion of the sulfur.
2. Vulcanization of raw rubber is always accompanied by an exothermic reaction.
3. There is a definite time interval between the endothermic and exothermic reactions.
4. The exothermic reaction increases proportionally to the amounts of sulfur used in compounding until the point of theoretical saturation is reached.
5. The time of starting of the exothermic reaction is not influenced by the proportion of sulfur but is uniformly the same.
6. There is no endothermic reaction after the vulcanization reaction has begun, and there is but one exothermic reaction during the vulcanization. The reaction does not proceed in steps.

The Thermal Decomposition of Natural and Artificial Rubber in the Presence of Aluminum Chloride

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The numerous published works on reactions taking place under the influence of aluminum chloride show more and more what an important part the latter plays in organic chemistry. During recent years experiments by one of the present authors and his collaborators have shown that aluminum chloride acts as a catalyst in the thermal decomposition of complex homogeneous substances, that it lowers the temperature of the decomposition and that it makes this decomposition take place in a well-defined way. This phenomenon consists of a hydrogenation by hydrogen of the unsaturated fragments of the decomposition, where the hydrogen is removed from the condensed mass of organic material. For example, a complete series of hydrocarbons of different composition and constitution are obtained by the decomposition of such substances as cholesterol,¹ oleic acid,² and abietic acid,³ in addition to phytosterols (betulin⁴).

These investigations showed that the chemical nature of the hydrocarbons formed differs according to the original substance.

Cholesterol, for example, yields, in addition to gaseous and easily volatile paraffins, a preponderance of benzene hydrocarbons in which cyclic forms (cyclohexane and cyclopentane derivatives) predominate. Therefore benzene from cholesterol resembles benzene from crude Caucasian oil. The properties of the hydrocarbons from the higher fractions are likewise different from those of the substances named above.

In contrast to cholesterol, there are formed in this manner, from oleic acid, paraffins and olefins, in the benzene fraction of which hexahydroaromatic forms are almost lacking.

There is a similar difference between the decomposition products of abietic acid and of betulin. In the first case aromatic products predominate, whereas in the second in the lower fractions hexamethylene and in the higher aromatic hydrocarbons predominate.

In the decomposition of paraffin oil and of solid paraffin,⁵ *i. e.*, of substances with open chains, a benzene was obtained which was almost free from cyclic hydrocarbons. In the decomposition of solar oil from Caucasian naphtha, which consists chiefly of condensed rings, there was obtained on the contrary a benzene rich in cyclic hydrocarbons of the polymethylene series.

The definite character of the decomposition products from homogeneous compounds as well as from petroleum oils shows that cracking under the influence of aluminum chloride results in a mixture of hydrocarbons, the nature of which depends upon the decomposition and structure of the substances which were cracked.

There is obviously a conformity to law, which makes it possible to learn the chemical nature of organic substances from their decomposition products.

This further study of the cracking effect of aluminum chloride on carbon com-

pounds shows the new part played by aluminum chloride in organic chemistry. Thus cholesterol, abietic acid, betulin, and naphtha oils yield decomposition products which conform to present concepts of the structure and chemical character of these complex compounds.

These results induced us to crack natural rubber in the presence of aluminum chloride in order to find out to what extent the decomposition products of this interesting high polymeric natural product, which is so important technically, agree with the prevailing views upon its structure.

Description of the Experiments

Natural rubber (pale crepe) of the following composition: moisture 1.2 per cent, ash content 0.6 per cent, resin 2.4 per cent, yielding 95.8 per cent of pure product, was used.

Fifty grams of rubber (86.37% C, 10.65% H), cut up fine and dried in a desiccator over sulfuric acid, were carefully mixed with 5 grams of finely powdered aluminum chloride and heated in a flask provided with a fractionating column. The reaction begins on slight warming, and proceeds with great rapidity and with almost explosive violence. The heating must be controlled because the rubber melts, and the decomposition ceases after about 5 minutes. A dark green condensate passed through a large condenser into a well cooled receiver; the gases were collected in a gasometer. With the object of ending the reaction and of removing the high boiling substance, the flask was heated in the luminous flame of a Bunsen burner. In this way, 200 grams of rubber were decomposed in several portions, from which 138 grams of the liquid product (69% of the rubber) were obtained. The amount of gas was 14 liters.

The mixture of hydrocarbons obtained was steam-distilled. Seventy-six grams passed over, which were dried with sodium sulfate and fractionated with the aid of a good fractionating column yielded:

		n_D^{18}
34-36°	1.5 g.
36-150°	34.0 g.	1.4201
150-200°	20.0 g.	1.4564
200-240°	14.0 g.	1.4791

All the fractions were saturated to permanganate.

The oil remaining in the flask was dried and distilled at 9 millimeters.

		n_D^{16}
70-170°	22 g.	1.5124
170-225°	36 g.	1.5390
225-250°	8 g.	1.5498

These oils decolorized permanganate.

When the quantity of aluminum chloride was increased to 20 per cent, the reaction was still energetic. Ninety grams of rubber and 18 grams of aluminum chloride yielded 54 grams of liquid condensate.

Fractionation over sodium gave the following results:

		n_D^{18}
34-36°	3 g.	1.3700
36-150°	19 g.	1.4190
150-220°	20 g.	1.4663
220-270°	7 g.	1.4928
270-300°	2.5 g.	1.5198

These fractions were all saturated to permanganate.

Seventy-five grams of the heavier oils obtained with 10 per cent aluminum chloride were once more decomposed with aluminum chloride (7.5 g.), from which 58 grams of condensate were obtained. This was washed with alkali, dried, and fractionated.

20-150°	9 g.	1.4100
150-200°	15 g.	1.4360
200-290°	30 g.	1.4938

All these hydrocarbons were wholly inert toward permanganate.

The benzene fractions of all the decompositions were combined and this rubber-benzene of a saturated character gave d_4^{20} 0.7465 and n_D^{15} 1.4203.

From this benzene, the following fractions were isolated and their hexahydroaromatic hydrocarbon contents determined.

		d_4^{20}	n_D^{15}
78-82°	2 g.	0.7001	1.3993
99-102°	6 g.	0.7310	1.4114
120-126°	10 g.	0.7655	1.4278
139-141°	2.5 g.	0.7818	1.4362

Analysis of the benzene (b. p. 70-150°) remaining after the separation of these portions gave:

0.112 g. substance: 0.3477 g. CO_2 ; 0.1472 H_2O
 C_8H_{12} calculated C 85.60 H 14.40 found C 85.27 H 14.71

To determine the content of hexahydroaromatic hydrocarbons, the fraction 70-150° obtained by dehydrogenation catalysis over platinized asbestos at 300° was studied. The dehydrogenated product gave d_4^{20} 0.7561. Fuming sulfuric acid (7%) absorbed 13 per cent of the aromatic hydrocarbon formed during catalysis.

Analysis of the product freed from aromatic hydrocarbons gave:

0.1169 g. substance: 0.3682 g. CO_2 ; 0.1506 g. H_2O
 C_8H_{12} calculated C 85.60 H 14.40 found C 85.86 H 14.41

These data prove that the fraction 70-150° contains, besides cyclohexane derivatives, still other cyclic hydrocarbons.

Among the narrower fractions of rubber-benzene, that of 120-126° was studied.

0.1008 g. substance: 0.3165 g. CO_2 ; 0.1310 g. H_2O
 C_8H_{12} calculated C 85.60 H 14.40 found C 85.67 H 14.54

Accordingly this fraction consists exclusively of cyclic saturated hydrocarbons. It was subjected to dehydrogenation over platinized asbestos at 300° C. There was an abundant evolution of hydrogen, and the product obtained showed a great increase in the refraction, viz., n_D 1.4436.

Fuming sulfuric acid (7%) absorbed from this 41 per cent of aromatic hydrocarbons (xylenes), which are formed by dehydrogenation of dimethylcyclohexane.

Judged by its constant, the fraction 99-102° must contain a certain quantity of methylhexamethylene, whereas the properties of fraction 139-141° approach those of the higher homologs of cyclohexane.

Analysis of the higher boiling rubber oils gave the following values:

150-200°: 0.1465 g. substance: 0.4647 g. CO_2 ; 0.1715 g. H_2O
 200-290°: 0.1644 g. substance: 0.5283 g. CO_2 ; 0.1778 g. H_2O
 found C 86.51, 87.64 H 13.09, 12.10.

The gaseous hydrocarbons formed by the cracking of pale crepe in the presence of aluminum chloride are likewise saturated to permanganate.

Therefore the mechanism of the decomposition of rubber under the influence of

aluminum chloride is different from dry distillation; no isoprene could be detected among the decomposition products.

Decomposition of Natural Rubber from the Plant "Tau-Sagis" (*Scorzonera Tau-Sagis*)

This dark, in fact almost black, rubber contained 1.5 per cent moisture, 2.4 per cent, resin and 1 per cent ash; its purity was therefore 95 per cent. The composition was similar to that of pale crepe, *viz.*, 85.49 of C and 10.11 of H.

Fifty grams of finely divided rubber were heated with 5 grams of aluminum chloride in the cold flame of the gas burner, as described above. At first only the evolution of gas was observed. Unlike that of pale crepe, the reaction is not energetic, so that heating was always necessary. In a receiver cooled with salt and snow, 35 grams of the liquid product were collected, that is, 70 per cent of the rubber used. In all 200 grams were used, from which 138 grams (69%) of liquid condensate and 17 liters of gas were obtained.

Sixty-four grams were collected by steam-distillation and gave the following fractions.

		n_D^{16}	d_4^{20}
22-150°	29 g.	1.4275	0.7404
150-200°	28 g.	1.4728	0.8411
200-235°	4 g.	1.4846	0.8485

All fractions reacted with permanganate, and thus differed from the hydrocarbons obtained from the decomposition of pale crepe.

The oil remaining in the flask was dried and fractionated at 15 millimeters.

		n_D^{17}
70-130°	16 g.	1.4888
130-180°	24 g.	1.5044
180-230°	16 g.	1.5170
230-250°	15 g.	1.5261

These fractions also decolorized permanganate. Sixty grams were decomposed with aluminum chloride, from which 36 grams (67%) of a mobile liquid condensate were separated as follows.

		n_D^{17}	d_4^{20}
30-150°	9 g.	1.4139	0.7426
150-200°	6 g.	1.4605	0.8425
200-267°	17 g.	1.4945	0.8848

These fractions did not react with permanganate, and therefore no longer contained unsaturated hydrocarbons.

The benzine fraction 22-150° (n_D^{16} 1.4275) of the first decomposition was hydrogenated over platinized asbestos, and the resulting catalysate had an n_D^{18} value of 1.4228. Such a slight drop in the refraction shows how poor this fraction was in unsaturated compounds.

Analysis of the completely hydrogenated benzine fraction gave:

0.1189 grams substance: 0.3716 g. CO_2 ; 0.1586 g. H_2O
 C_nH_{2n} , calculated C 85.60 H 14.40 found C 85.21 H 14.92

from which it follows that this fraction consists of cyclic forms with a slight admixture of paraffin hydrocarbons.

From the benzine obtained from the decomposition of rubber *Tau-Sagis*, the fraction 120-126° (n_D^{24} 1.4237; d_4^{20} 0.7594) was separated and dehydrogenated over platinized asbestos; the catalysate collected showed a considerable increase in the

refraction (n_{23} 1.4415; d_4^{20} 0.7904), which indicated the formation of aromatic hydrocarbons (xylene). Fuming sulfuric acid (7%) absorbed 33 per cent of the aromatic hydrocarbons formed. The residue freed from aromatic compounds showed the following constants: n_{24} 1.4226 and d_4^{20} 0.7445.

0.1160 g. substance: 0.1502 g. H_2O (CO_2 lost)
 $C_{10}H_{16}$ calculated H 14.40 found H 14.48

Therefore in the decomposition of this rubber as well, still other cycloalkanes besides the hexahydroaromatic alkanes are formed.

The fraction 150–200° and those of higher boiling points are pale yellow, react with permanganate, and have a distinct terpene odor, by which they are sharply distinguished from the hydrocarbons of the corresponding fractions obtained from the decomposition of pale crepe.

The portion 174–176° was separated from fraction 150–200° (n_{16} 1.4728) of the first decomposition. This reacted strongly with permanganate, and its analysis approached that of dipentene.

The gases from the decomposition of *Tau-Sagis* rubber reacted weakly with permanganate.

Decomposition of Synthetic Rubber

One hundred grams of finely divided synthetic rubber obtained by polymerization of butadiene with metallic sodium were mixed with 10 grams of aluminum chloride in a flask provided with a fractionating column. The reaction commenced very violently when heated over the luminous flame of a gas burner, and then continued without further heating. An abundance of gas was developed, and the temperature of the escaping vapors increased rapidly from 30–160°. The reaction had continued thus for about 5 minutes when a yellowish, mobile liquid collected in the cooled receiver. The gases were conducted through a washer with acidified permanganate solution, which was gradually decolorized. Further decomposition was carried out with heat until the temperature of the escaping vapors rose to 200°, at which point the heavy oil was driven over without the fractionating column.

One hundred grams of rubber gave 72 grams of condensate. In this way 375 grams of rubber in all were decomposed and 270 grams of condensate were collected, washed with alkali, then dried, and distilled. At 40–150°, 101 grams were obtained, and from 150–200°, 56 grams. These fractions with a wide boiling range reacted weakly with permanganate.

The heavy oil remaining behind in the flask, the quantity of which was 100 grams, was mixed with 10 grams of aluminum chloride and decomposed again, whereby 18 grams were obtained at 40–150°, 17 grams at 150–200°, and 60 grams at 200–285°. These fractions did not react with permanganate.

The benzine fraction (40–150°) from the first decomposition was divided into 2 parts: 35–70°, 13 cc., n_D^{16} 1.3832; and 70–150°, 80 cc., n_D^{16} 1.4205.

The fraction 70–150° was hydrogenated at 165° over platinized charcoal. The saturated product obtained showed the following constants: d_4^{20} 0.7442 and n_D^{16} 1.4162. The slight decrease in the refraction indicates that this fraction was not rich in unsaturated hydrocarbons. This was separated into two parts: 99–100° n_D^{16} 1.4112, d_4^{20} 0.7429, and 119–125° n_D^{16} 1.4205, d_4^{20} 0.7610. Their constants indicated that these fractions contained considerable quantities of cyclohexane hydrocarbon, which was saturated by dehydrogenation over platinized charcoal at 300°.

The catalysate from the first fraction had d_4^{20} 0.7687, n_D^{16} 1.4339, that from the second fraction: d_4^{20} 0.7892 and n_D^{16} 1.445.

To establish the presence of benzine hydrocarbons in the dehydrogenated mix-

ture, their behavior upon bromination in the presence of aluminum bromide was studied. In both cases an abundant crystallization of aromatic perbromides was obtained; the perbromide from fraction 99–100° fused at 254°, and was pentabromotoluene admixed with a little tetrabromoxylene, which accounted for the lower melting point. Pentabromotoluene melts at 283°.

The perbromide from the dehydrogenated fraction 119–125° after recrystallization from toluene fused at 256°, which indicated tetrabromoxylene. The mixture with the perbromide prepared from *p*-xylene had the same melting point. The hydrogenated benzene fraction 70–150°, from which the fractions 99–100° and 119–125° were separated, showed almost no change in its original properties; it had n_D^{18} 1.4153 and d_4^{20} 0.7440. When dehydrogenated over platinized charcoal at 300°, it yielded, along with an abundant liberation of hydrogen, a product of greatly increased refraction: n_D^{16} 1.4364. This indicates that there is also formation of large quantities of aromatic hydrocarbons. The product was freed from these by treatment with fuming sulfuric acid. The residue was washed with alkali, dried, and analyzed after distillation as follows: n_D^{18} 1.4183.

0.0858 g. substance: 0.2701 g. CO₂; 0.1094 g. H₂O

C₈H₈ calculated C 85.60 H 14.40; found C 85.85 H 14.27

These data show that considerable quantities of cyclic hydrocarbons which do not belong to the cyclohexane series remain in the benzene (70–150°) used in this dehydrogenation.

The benzene fraction 40–150° which, as described above, had been obtained by cracking the heavy oil from the first decomposition of butadiene-rubber proved to be identical chemically with that just described.

The fraction of the heavy benzene (150–200°), which was of a slightly unsaturated character, was oxidized with potassium permanganate in acid solution and was dried. It boiled within the same range d_4^{20} 0.8119, n_D^{18} 1.4582; 0.0976 g. of substance: 0.3062 grams CO₂; 0.1219 g. H₂O

C₈H₈ calculated C 85.56 H 14.40 found C 85.56 H 13.97

From this it follows that the high boiling hydrocarbons also consist preponderantly of cyclic compounds. Accordingly natural and artificial rubbers give the same results, and the similarity in the final decomposition products is doubtless closely related to a similar mechanism in the polymerization of the two substances.

Especially important seems to be the question of the manner of formation of the cyclic compounds which are formed in such large proportions in the hydrocarbons obtained by the decomposition of rubber with aluminum chloride. It might be thought that the polymerization of the diene hydrocarbons precedes their cyclicization, in which case there is first of all association of these ring compounds to rubber.

At the present time there is no unanimity of opinion regarding the structure of rubber. Some investigators (Weber and Staudinger) hold the view that the high polymeric rubber molecule contains long open carbon chains of isoprene molecules. Others agree with Harries that rubber represents a condensation product of isoprene to dimethyleyclooctadiene, which then undergoes an extensive polymerization. Harries and Evers later introduced the idea of a ring with seven or eight isoprene members.

The experiments on the decomposition of rubber with aluminum chloride show the completely different behavior of rubber under these conditions from its behavior during dry distillation. Recently Midgley and Henne⁶ destructively distilled a large quantity (200 lbs.) of rubber and obtained yields of 10 per cent of isoprene and 20 per cent of dipentene, together with small quantities of other hydrocarbons of the most varied structure and composition from C₆ to C₁₀. The yields of these

latter varied according to whether the distillation was carried out in the presence or in the absence of zinc oxide or magnesium.

The destructive distillation of rubber can naturally form isoprene as well as other products from cyclic structures.

The decomposition of rubber by aluminum chloride is a wholly different phenomenon; the process takes place at a much lower temperature, and isoprene is not formed, but on the other hand saturated light hydrocarbons of the benzene type as well as heavy oils the greater part of which are saturated. The decomposition of rubber in this case has the same mechanism as that of cholesterol and other homogeneous substances, and of petroleum products which were studied by Zelinsky and his collaborators (*loc. cit.*).

If we look forward to a time when petroleum is exhausted and in which chemical industry has consumed all the cheap light and heavy burning oils obtained from fossil natural products, it may perhaps be found that a burning oil can by that time be prepared by the cracking of natural rubber with aluminum chloride.

References

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- ² *Ber.*, **60**, 1793 (1927).
- ³ *Ber.*, **61**, 1054 (1928).
- ⁴ *Ber.*, **64**, 2132 (1931). The formula $C_{24}H_{40}O_2$, which Traubenberg (*Thesis*, Moscow 1917) proposed for betulin was later changed to $C_{26}H_{40}O_2$ by Dischendorfer (*Ber.*, **55**, 3692 (1923)).
- ⁵ *Nephtjanoe and Slanzewoe Chosjaistwo*, Moscow, No. 8 (1920), No. 3 (1921).
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Rubber and Thioglycolic Acid

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Based on its behavior toward halogens, hydrogen halides, nitrous acid, ozone¹ and hydrogen,² rubber has one double bond for each C_6H_8 group. One would therefore expect that it would be possible to obtain from the addition products of these substances new compounds which would throw considerable light on the constitution of rubber. With the exception of the ozonides, however, this is true only to a very limited extent, a fact which depends in part upon the almost complete lack of water-soluble derivatives suitable for further reactions. It is true that the bromide of rubber can be converted by phenols into alkali-soluble compounds,³ but the carbon bonds of the compounds appear to be formed not only between the components⁴ but also by a closing of the ring within the rubber skeleton.⁵ Moreover in the transformation of the bromide by triethyl phosphine^{6,6} cyclization appears to take place. In view of this, the constitution of these derivatives indicates that further work with them would be to little purpose, and as a matter of fact until now almost nothing of any great interest has appeared.

For some years past a renewed study of thioglycolic acid and its behavior toward various substances has been made by the author, and this acid was allowed to act upon rubber, under which conditions it was expected that water-soluble addition products would be obtained in the form of alkali salts. Such compounds were in fact actually obtained. When a sample of plantation pale crepe with a large quantity of thioglycolic acid was kept for 16 months at room temperature, the greater part of the mixture dissolved in normal sodium hydroxide solution. From this solution there was obtained by precipitation with hydrochloric acid a substance which, after several purifications, had the composition $C_6H_8(HSCH_2CO_2H)_{0.953} - H_{0.053} + O_{0.014}$ and an equivalent weight of 165.5, while the sulfur content corresponded to an equivalent weight of 163.7. Since the composition agreed very closely with the formula $[C_6H_8SCH_2CO_2H]_x$, experiments were then made to ascertain in what way various factors, *e. g.*, the time of the reaction, proportions of the ingredients, temperature, solvent, and preliminary treatment of the rubber influence the reaction of the latter with thioglycolic acid. Finally, to complete the work a few experiments were also carried out with balata and gutta-percha. In general, balata behaved like rubber, whereas the reaction of gutta-percha and thioglycolic acid was hardly appreciable. These experiments were of course carried out with less well defined materials, but nevertheless they seem to the author to conflict with the idea that balata and gutta-percha are identical and are geometric isomers of rubber.⁷

Description of Experiments

In May, 1930, pale crepe in strips 1 cm. long and 1 mm. thick (3 g.) was treated with thioglycolic acid (9 g.). The mixture was allowed to stand at room temperature, under which conditions the liquid gradually thickened and the shape or outline of the strips which were still undissolved became indistinct, perhaps because of light refraction, so that after a few months the mixture appeared to be almost homogeneous. In September, 1931, the product was stirred thoroughly with normal sodium hydroxide in several portions, as a result of which 0.65 gram of opaque frag-

ments of the original strips remained undissolved, while the solution obtained was only slightly opalescent. This solution was diluted with water and treated with hydrochloric acid, as a result of which an emulsion was first formed, following which a voluminous, white plastic and somewhat elastic mass separated. Upon extraction with ether the aqueous mother liquor yielded 5.5 grams of a colorless liquid (thioglycolic acid), while after pressing and superficial drying the separated substance weighed 10 grams. This mass, which accordingly had a high water content, was again dissolved in very dilute sodium hydroxide, was again precipitated with hydrochloric acid, was washed by kneading with pure water, was pulled out into thin sheets and was dried, first in the air and finally *in vacuo* over phosphoric anhydride, under which conditions it gradually became vitreous or resinous. The vitreous mass was pulverized, and after prolonged drying to constant weight the powder was analyzed:

0.2106 g. substance (0.2099 g. ash-free): 0.4089 g. CO_2 , 0.1425 g. H_2O .
0.3884 g. substance (0.3872 g. ash-free): 0.5521 g. BaSO_4 (Klason combustion) and 0.0012 g. ash.

0.2081 g. substance (0.2074 g. ash-free): after solution in 0.1157 *N* NaOH and back-titration with 0.1 *N* HCl (phenolphthalein), 10.83 cc. NaOH.

	Calculated	C	52.45	H	7.55	S	20.02	Equiv. Wt.
Found		53.13		7.60		19.58		160.15
								165.5
		$\text{C}_5\text{H}_8\text{SCH}_2\text{CO}_2\text{H}$ or $\text{C}_7\text{H}_{12}\text{O}_2\text{S}$ (160.15)						

As mentioned in the beginning, the analyses correspond arithmetically to the formula $\text{C}_5\text{H}_8(\text{HSCH}_2\text{CO}_2\text{H})_{0.933} - \text{H}_{0.053} + \text{O}_{0.014}$. The preparation which was analyzed was converted at about 75–80° C. into a tough viscous mass, and tiny gas bubbles became visible at about 110° C. The preparation was converted by alcohol into a sticky mass from which, upon heating, a slightly opalescent solution was formed. Upon cooling this solution did not change, but upon spontaneous evaporation it left behind a sticky rubber-like residue. The behavior of the product toward acetone and glacial acetic acid was practically the same as toward alcohol. It was not altered by carbon tetrachloride or benzene at ordinary temperature, and upon heating in these solvents it changed to a pasty mass, but hardly went into solution at all. With dilute solutions of calcium, barium, zinc, cadmium, aluminum, lead, mercuric and silver salts, a product prepared with 0.1 *N* sodium hydroxide gave in a solution, neutral to phenolphthalein, cheesy or jelly-like precipitates which upon heating were converted into amorphous powders. With magnesium sulfate no solution was obtained, and upon spontaneous evaporation the solution of the sodium salt was converted into a rubber-like, ultimately vitreous mass, which upon solution in water and addition of alcohol formed a milky mixture, from which a pasty mass separated.

In October, 1931, seven new experiments were started with the same crepe, which was now a year and one-half old. Five grams of rubber in strip form were treated with the same quantities of thioglycolic acid, and after the times designated in Table I the mixtures were treated in the same way as in the previous experiment. The weight of the undissolved, more or less deformed, and eroded strips which were recovered, and which were stuck together after drying in the air, are given in Table I under the heading "Rubber Recovered." The yields of the thioglycolic acid compounds, which resembled the preparation above, are itemized under the heading "Yield." The compositions of these compounds are expressed by the coefficients in the formula: $\text{C}_5\text{H}_8(\text{HSCH}_2\text{CO}_2\text{H})_x + \text{H}_x + \text{O}_x$. The equivalent weights obtained by alkalimetric titrations, and based on the sulfur contents, are also included.

TABLE I

Time in Months	Rubber Recovered, G.	Yield, G.	<i>t</i>	<i>h</i>	<i>o</i>	Equivalent Weight Found	Equivalent Weight Calculated
0.5	3.8	2.4	0.7745	0.222	0.232	181.0	185.1
1	3.6	2.5	0.797	-0.626	0.244	176.2	181.5
2	3.3	3.2	0.737	-0.662	0.367	184.4	191.5
3	3.1	3.6	0.7655	-0.473	0.134	183.7	183.2
4	3.1	3.6	0.7785	-0.263	-0.007	178.4	179.0
5	3.1	3.6	0.805	-0.456	0.237	178.8	180.8
6	3.1	3.75	0.808	0.116	0.161	181.7	179.8

The data show that the reaction is fairly rapid at first and then gradually becomes very slow, so that the sulfur content, that is, the thioglycolic acid content, in the reaction product increases to only a slight extent. There is, of course, a certain danger from autooxidation of the products during the process, but this difficulty was disregarded for the time being. In an experiment with twice the proportion of thioglycolic acid, 5 grams of the same crepe as that used before left after one month 3.1 grams of unchanged substance, and yielded 3.8 grams of reaction product of the composition $C_5H_8(HSCH_2CO_2H)_{0.825} + H_{0.564} + O_{0.026}$ and an equivalent weight of 176.7, compared with a calculated value of 176.5.

The possibility of making a sample of rubber react completely by repeated treatment with thioglycolic acid was studied in a separate series of experiments. The portions of the substance recovered after the various treatments, and washed with alcohol after each treatment, were let stand anew each two weeks with the same quantities as before of fresh thioglycolic acid.

TABLE II

Thioglycolic Acid, G.	Rubber Recovered, G.	Yield, G.	<i>t</i>	<i>h</i>	<i>o</i>	Equivalent Weight Found	Equivalent Weight Calculated
5	3.8	2.4	0.7745	0.222	0.232	181.0	185.1
5	2.5	2.1	0.823	-0.131	0.147	177.4	177.5
5	1.4	1.9	0.877	-0.054	0.148	171.1	172.4
3	0.6	1.4	0.870	0.038	0.117	170.3	172.5
2	...	1.1	0.876	0.219	0.124	169.0	172.3

It was possible, therefore, to transform practically all of the sample into rubber-thioglycolic acid compound, and a change in the ratios during the various treatments was not observed.

In experiments with heat, 5 grams of crepe were again treated as above with thioglycolic acid, but at 110°. The results obtained are given in Table III.

TABLE III

Time in Hours	Thioglycolic Acid, G.	Rubber* Recovered, G.	Yield, G.	<i>t</i>	<i>h</i>	<i>o</i>	Equivalent Weight Found	Equivalent Weight Calculated
16	5	5.4	0.5	0.563	-0.478	0.220	215.4	218.4
6	10	4.9	1.1	0.681	-0.193	0.189	192.4	196.2
12	5	3.4	2.0	0.650	-0.733	0.228	198.4	201.2
12	5	...	1.5	0.548	-0.296	0.151	217.5	220.0

* The substance recovered was always tackier and more difficult to handle, and its weight was obviously wrong on account of various factors.

As the data show, the reaction proceeds more rapidly at higher temperatures, and at the same time the ratios become surprisingly irregular, which may depend among other reasons upon an adhesion of the rubber strips and upon the resulting difficulty in the reaction between the various reagents.

In experiments with glacial acetic acid as solvent for the thioglycolic acid compound which was formed, the presence of acetic acid was found to be of no advan-

tage. If, however, all that is desired is an incompletely formed product from the thioglycolic acid, then benzene solutions may be suitable. In an experiment under these conditions there were obtained after two weeks, for example, 4.4 grams of a product resembling masticated rubber from 5 grams of crepe and 10 grams thioglycolic acid in 100 cc. of benzene. This product had the composition $C_5H_8(HSCH_2CO_2H)_{0.260} - H_{0.479} - O_{0.033}$, and an equivalent weight of 336.0 (calculated 350.0).

In experiments with samples of masticated rubber, two representative specimens of a shipment of crepe which had just been received at the factory were milled by Dr. Hagman for 10 and 25 minutes at about 70°. Five grams of untreated material and five grams of each of these two samples were let stand for one month at ordinary temperature with twice the quantity of thioglycolic acid. Table IV gives the quantities and compositions of the rubber-thioglycolic acid products obtained from the mixtures.

TABLE IV

Time of Milling, Minutes	Yield, G.	<i>t</i>	<i>h</i>	<i>o</i>	Equivalent Weight Found	Equivalent Weight Calculated
0	3.7	0.860	0.062	0.138	171.1	173.9
10	3.5	0.878	-0.206	0.089	169.1	171.1
25	3.5	0.873	-0.228	0.161	170.4	172.7

Except for differences in the hydrogen contents, which possibly lie within experimental error, there is according to these results no difference evident in the behavior of the masticated rubber and that of the untreated rubber toward thioglycolic acid. Noteworthy also is the agreement between these experiments and similar ones previously carried out with much older crepe.

In experiments with crude balata, a mixture of 5 grams of balata and 10 grams of thioglycolic acid was first of all let stand for 1 month at ordinary temperature. The mixture was then stirred thoroughly with caustic soda, and the alkaline solution obtained gave with hydrochloric acid first an emulsion and then an extremely fine-grained precipitate, which could be filtered after a fashion only after it had been warmed for 1 hour on a water bath. Its weight was 1.1 gram, and after reprecipitation in the usual way its composition was $C_5H_8(HSCH_2CO_2H)_{0.729} - H_{0.340} + O_{0.262}$. Of the undissolved material, 3.1 grams were again let stand for 1 month with 8 grams of thioglycolic acid, after which 2.4 grams were recovered, while 1.0 gram of a reaction product was obtained, which had the composition $C_5H_8(HSCH_2CO_2H)_{0.661} + H_{0.043} + O_{0.217}$, and an equivalent weight of 197.0 (calculated 200.4). Upon renewed treatment of the still undissolved strips with 5 grams of thioglycolic acid, but this time for 6 hours on a boiling water bath, 1.4 gram of balata remained undissolved on treatment with alkali, while the alkaline solution yielded 1.0 gram of an amber-colored substance which could not be pulverized, and which had the composition $C_5H_8(HSCH_2CO_2H)_{0.411} - H_{0.022} + O_{0.141}$.

Some experiments were also carried out with four samples of gutta-percha, *viz.*, crude gutta-percha in block form and in sheet form and pure gutta-percha in flake and in ribbon form. As before, 5 grams of the gutta-percha and 10 grams of thioglycolic acid were let stand for 1 month at ordinary temperature. This treatment gave with aqueous caustic soda blood-red solutions, and left the original material undissolved in a more or less disintegrated state. The undissolved products, after drying in the air, weighed several per cent more than previously. With hydrochloric acid the solutions showed slight emulsification. In three cases however there were only traces of precipitates, and these could not be filtered, while in one experiment 0.2 gram of a gritty powder separated.

The samples of rubber and balata which were used in the investigation were ob-

tained through the courtesy of Dr. S. Hagman, Hålsingsborgs Gummifabriks A.-B., and the gutta-percha samples from H. Rost & Co., Hamburg. All the elementary analyses were carried out by my assistant, R. Windladh.

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Heat Treatment and Polymorphism of Gutta-Percha and Balata

J. N. Dean

Gutta-percha in its genuine form as received from the native collectors consists of about 75 per cent of hydrocarbon, 10 per cent of resin, 5 per cent of so-called "dirt," and the remainder water. The "dirt" is made up of mechanical contamination and serum products peculiar to the particular latex. Balata as received from South America is composed of similar components to those of gutta-percha, though the quantity of dirt and resin is much greater and the hydrocarbon correspondingly less. In the best qualities there is about 40 per cent only of hydrocarbon, nearly an equal amount of resin, and the rest, moisture and dirt, the latter being up to 15 per cent in amount.

Preparation of Pure Hydrocarbon.—The hydrocarbon of either gutta-percha or balata can be obtained easily by solution in a suitable petroleum spirit, removal of the insoluble matter by filtration, and precipitation of the hydrocarbon by refrigeration of the solution at a temperature of about 0° C. At this temperature the hydrocarbon is insoluble in the solvent, but the resin remains dissolved. The white flakes of hydrocarbon are removed from the resin solution and washed with clean cold spirit and dried. The last traces of resin may be removed more completely by soaking the porous flakes in acetone.

The hydrocarbon is intensely susceptible to oxidation, and this is accelerated by light and air. Oxidation during the preparation of the hydrocarbon may, however, be entirely eliminated by expediting the operations, by screening from light, by removal of oxygen from the apparatus, and by ensuring that the solvents used are first freed from dissolved oxygen and from peroxides. The importance of these details cannot be overemphasized, since the hydrocarbon is considerably altered in its properties when only very slightly oxidized. Such factors as plasticity, resilience, stickiness, softening point, ease of solubility in solvents, and, most important of all, aging properties can be strongly affected where oxidation is so slight that it cannot be detected by normal chemical means. Owing to lack of attention to these details, many experimental results have been entirely vitiated and a considerable proportion of the literature, scant as it is, on the subject of purified gutta-percha has thereby been rendered valueless.

Discovery of Effect of Heat Treatment of Gutta-Percha.—The fact that the properties of gutta-percha were profoundly altered after being subjected to heat treatment was discovered by accident. Some experiments were in progress to determine the density of a sample of gutta-percha hydrocarbon at different temperatures. The density was measured at increasing temperatures up to 70° C., and in order to check the measurements they were repeated as the temperature decreased. At each determination the temperature was kept constant for some considerable time in order to allow of even distribution throughout the specimen. Unconsciously the sample was being heat-treated at each stage, and it was discovered that the cooling-density curve did not coincide with the heating curve. Fears that a constant error was creeping in were eliminated, and the phenomenon was confirmed by many subsequent measurements. The form of the curve is given in Fig. 1, and is typical for every sample of gutta hydrocarbon examined from whatever the source. Simple

considerations soon showed that the change in density must be coupled with a change of phase.

The experiments were followed by still more precise methods, using a dilatometer, and the results were even more surprising.

The dilatometer containing the specimen of hydrocarbon was immersed in a bath, which was fitted with a quick adjusting thermostat. The height of the liquid in the capillary was observed at regular intervals of a few minutes until it was steady, and the temperature of the bath was then quickly raised by $1/2^\circ\text{C}$. and kept constant. The resulting expansion of the contents of the dilatometer bulb was then observed by noting the rise and fall in the capillary until again constant. Above 49°C . the temperature of the bath was raised by one degree at a time, but except for this the operations were repeated at each succeeding change of temperature until the end of the experiment.

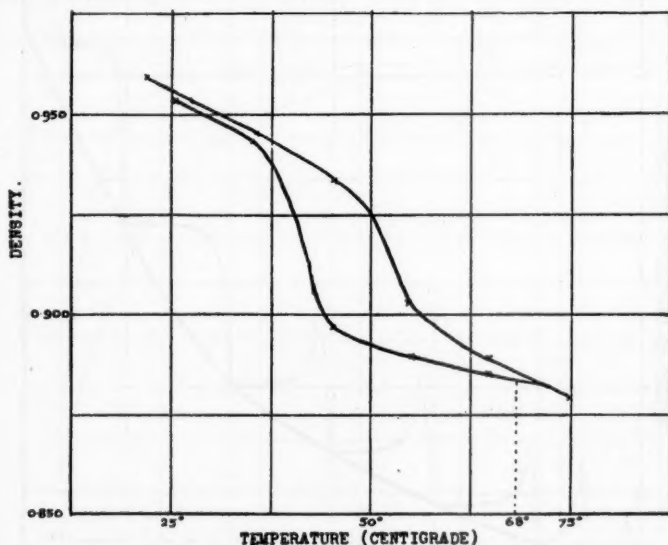


Figure 1

By careful observation of the expansion during the whole time, it was observed that a hump appeared in the dilation-temperature curve at each change in temperature (see Fig. 2), and it seemed that either the sample was dilating to a certain point and then contracting to a phase of higher density, or that energy was being liberated in the specimen by transition from one phase to another of lower energy content. This energy would heat the surrounding fluid to a temperature higher than that of the bath, and would cause a rise in the capillary above that due to the natural combined expansion of the sample and fluid caused by the prescribed temperature change. Experiments carried out at a later date have demonstrated the probability that both these causes are contributory to the humps in the curve, but an account of these experiments need not be enlarged at this stage. Further inspection of Fig. 2 will reveal another peculiarity. It will be seen that at and above 52°C . the humps no longer appear, and the expansion occurs normally. This temperature then would seem to be a change point, and as will be seen later corresponds approximately with what may be termed the softening point of the β modification. The thick line in Fig. 2, which makes the stable density-temperature curve, has an in-

flection which occurs at the same point, namely, $52^{\circ}\text{C}.$, and this constitutes further evidence of the existence of a change occurring.

A separate unrelated series of experiments was carried out to determine the accelerated aging effect of warm air upon some specimens of washed and dried gutta-percha, and the temperature chosen was one that had been found by experience to be satisfactory, namely, $46^{\circ}\text{C}.$ It was observed that the samples were distinctly soft after a short time of heating, but that after several hours had elapsed they had hardened to about the same degree as a duplicate set at air temperature. At first this was wrongly connected with the commencement of aging, but as no other indications of oxidation or deterioration were apparent at this stage, it was considered worthy of further investigation.

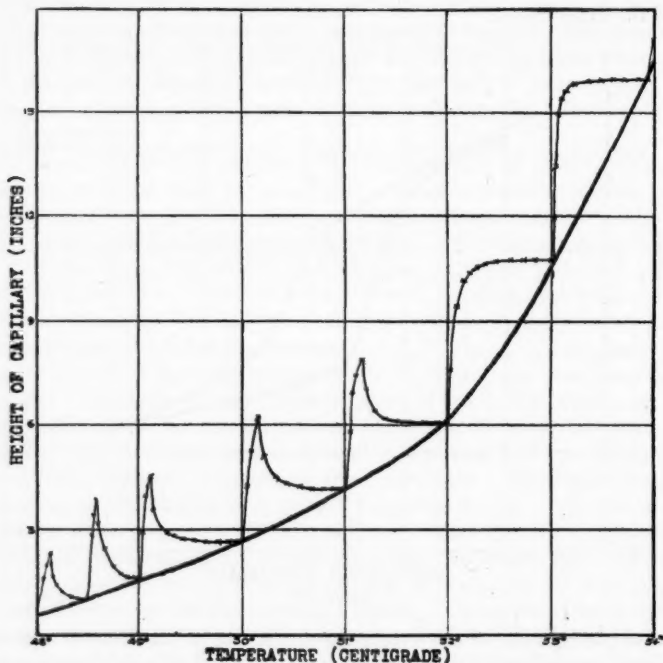


Figure 2

With the object of eliminating the possibility of the gutta-percha being altered by oxidation, and, in order more rapidly to heat the specimens to the desired temperature a bath of water was maintained thermostatically at $46^{\circ}\text{C}.$ and the phenomenon confirmed. Specimens of gutta-percha were immersed and periodically examined. After a few minutes they were sufficiently soft to be capable of being squeezed between the fingers, and the degree of softness varied from sample to sample, and was roughly proportional to the resin content. At the end of about one hour's heating they had hardened materially, and after a further hour were about as hard as the cold samples.

Upon raising the temperature a few degrees, to about $50^{\circ}\text{C}.$, the pieces of gutta-percha became soft once more, and upon maintaining them at this temperature for several hours they re-hardened as before. Attempts to continue this process at higher and higher temperatures failed, and it was soon realized that a "limiting"

temperature existed, above which the hardening failed to occur. This limit was carefully investigated, and it was found to vary with the resin content, being higher the less the resin. Furthermore, it was found that when an unheated specimen was heated directly to a point just below the limiting temperature, it hardened relatively rapidly; but that if it was subsequently heated to a temperature just above the limit, it softened at once; and, finally, it was observed that if this specimen was now cooled to the previous temperature, that is just below the limit, it was no longer hard, but could be re-hardened by maintaining the temperature for the pre-determined time. It is clear that the "limiting" temperature is a transition point of some sort, and that gutta-percha is polymorphic. The fact that increasing quantities of resin lower this point indicates that the phase change is occurring in the hydrocarbon portion of the gutta-percha, and that the resin, acting as a solvent, is lowering the melting point. Originally, these two modifications were termed A

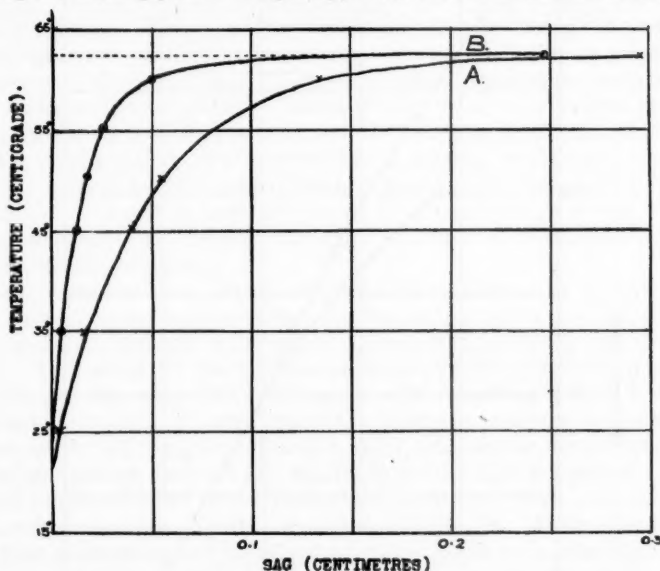


Figure 3

and B, respectively, but letters α and β will be used in this paper. The β modification is that which is formed when gutta-percha is prepared in the usual way, and the α variety that which is obtained by heat treatment.

Details of this process of heat treatment and the changes produced in the gutta-percha were first described in a British Patent (Smith, Garnett, and Dean, British Patent 326,481 (1928)). Full information on the methods adopted will be referred to later.

Effect of Heat Treatment upon Properties.—As has been indicated already, the effect of heat treatment is undone by heating the sample to a point above the limiting temperature, so that a comparison of normal with heat-treated gutta-percha must be made at temperatures below this temperature.

Softening Point.—One property of gutta-percha which is exceedingly important, and which is dependent upon its quality, is the plasticity. However, as this is only of interest at temperatures above the melting point of the substance, it is not suitable as a means of following the heat treatment. A closely related mechani-

cal property of gutta-percha is its softening temperature, and the profound effect of heat treatment upon this property has already been described. For a more definite comparison, however, it was necessary to utilize a more precise method of measurement than that of squeezing between the fingers. The method adopted is in reality dependent on the effect of temperature upon the tensile properties of the material. It is carried out upon a specimen of the sample which has been pressed to a bubble-free sheet of 0.006 inch thickness. This is tied over the end of an open glass tube of 10-mm. internal diameter and 1.5-mm. wall thickness, and the sheet is made to adhere to the outside of the tube by means of a hot iron tool. The gutta-percha bag, so formed, is made to carry a load of 20 gr. of mercury, and is clamped in a bath of water so that the surface of the gutta-percha is 2.5 cm. below that of the water. The bath of water is heated so that its temperature is raised at

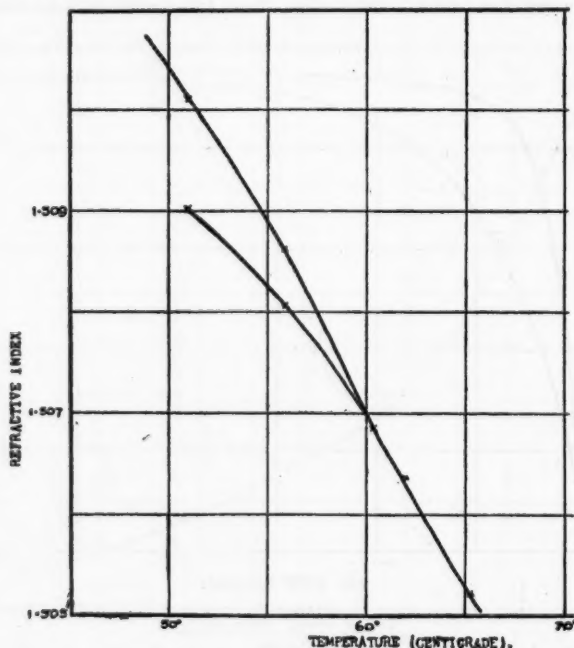


Figure 4

a rate of 2° per minute, and the amount of sag of the gutta-percha bag is measured at suitable intervals by observation through the eyepiece of a vertically traveling microscope. The degree of sag is plotted against the temperature, and the curve will be found to have the form of that of A in Fig. 3. If now a determination is made upon a heat-treated specimen, a curve similar to that of B will be obtained. The important point of difference between A and B is that, though the final softening point is unaltered, the strength of the heat-treated specimen at any temperature below the softening point is very much greater than that of the normal one, and that the former passes through a relatively sudden change at its true softening point. It is probable that the difference between the two is even greater than is apparent from this comparison, since the normal specimen is receiving a sort of rapid heat treatment during and incidental to the experiment, and that by the time the true softening point is reached the two samples are in a similar condition.

Density.—A definite, though slight, permanent change in the density of different varieties of gutta-percha and balata hydrocarbon is apparent from the following figures. The column headed normal is the density of a sample as prepared by careful solution, filtration, and precipitation; that marked heat-treated is after submission to a temperature of 60° C. for two hours. It will be clear from later experiments that this time and temperature of heat treatment is not enough to render the change complete, but at the time these experiments were made, knowledge of the subject was incomplete.

Source of Hydrocarbon	Density d_4^{25}	
	Normal	Heat Treated
Balata sheet	0.9475	0.9544
Balata block	0.9434	0.9528
Leaf plantation gutta-percha	0.9459	0.9497
Gutta-percha (Isonandra)	0.9434	0.9478

Refractive Index.—The refractive index-temperature curves of gutta-percha hydrocarbon show peculiarities which offer further evidence of its polymorphism. An inspection of the curve (Fig. 4) discloses an optical anisotropic condition that occurs at temperatures below 60° C. down to temperatures at which the specimen becomes too opaque to make a measurement. This double refraction is presumably due to the presence of the two modifications co-existent in the mass; no doubt, if the sample were to be fully heat-treated, it would be converted entirely into the α modification. A sample consisting purely of one modification would obviously be single phased and would therefore no longer exhibit this effect unless the material were itself double refracting.

Stability.—Owing to the soft nature of the resins in some of the raw products, there is formed on the surface of the manufactured article an exudation of sticky or oily substance especially if the article is under strain, such as that produced by bending. This exudation renders the material unstable and there appears to be some evidence that where the resin exudes, the remaining sample is capable of absorbing more water. Whether or not this is true the heat-treated specimens can be preserved for very long periods under water, whereas the normal specimens are liable to turn spongy and soft and rapidly to oxidize and decompose.

A most important effect in this connection is observed when compositions other than pure gutta-percha or balata are under consideration. It has always been observed that substances may be added to gutta-percha or balata which cause an improvement in their electrical values, but that after a time they tend to bloom or exude in the same manner as balata resin. In some cases this occurs so badly that the whole or nearly all of the added substances will creep to the surface in the course of time. In many of these cases a heat-treatment will entirely prevent this and, in a particular instance, it has made possible the use of K.-gutta, a substance which has unique properties for submarine cable insulation.

A paper (J. N. Dean, *India Rubber J.*, **82**, 853 (1931)) describes the development, manufacture, and use of this K.-gutta, which is composed of gutta-percha and balata, specially prepared to remove all substances harmful to the attainment of the best electrical properties, admixed with petroleum jelly and, if desired, specially deproteinized rubber.

The heat-treatment of the K.-gutta is also described, and the paper concludes with data on its mechanical and electrical properties, and finally a comparison of its resistance to aging and water absorption with that of normal gutta-percha.

The substances which have been called K.-gutta are protected by patents among which British Patent 346,382 (1929) may be cited for reference.

Tensile Curve.—The tensile properties of gutta-percha or balata are but slightly

altered by heat treatment, the only obvious effects being a tendency to raise the yield point slightly to render the load required for yield more constant over the range of yield and to lower the final elongation to a small extent.

Solubility.—It has been found that the solubility of the α variety is lower than that of the β , but that this does not constitute a means of separating the two, because other factors also affect the solubility.

It has only recently become known that gutta-percha can be separated into two fractions by means of solvents (see Smith, Garnett, and Dean, British Patent 343,510 (1929)).

A suitable solvent is benzene, and the fractionation temperature is 19° C. Petroleum spirit is also capable of fractionally dissolving the hydrocarbon, but the temperature varies with the boiling point and other properties of the spirit used. On account of the fact that the part that is soluble in benzene at 19° C. is of poorer quality than the insoluble portion, the two products have been named grade II and I, respectively, though it must be remembered that the differentiation is quite arbitrary and is only fixed by the temperature (namely, 19° C.) which has been found convenient. If a higher temperature is used more will dissolve, and at about 25° C. the whole of the gutta is soluble.

It is found that the effect of the heat-treatment on the solubility renders the so-called grade II variety quite insoluble at 19° C.

If the resin has been removed from a sample by boiling in acetone, the gutta-percha will be partially converted to the heat-treated or α condition, because acetone boils at 57° C. This gutta-percha should be boiled in water and chilled, preferably by passing between cold rolls, before being fractionated. The heating and quenching will convert it to the β variety.

Effect of Heat-Treatment upon Structure.—The x-ray analysis of the hydrocarbon from balata or gutta-percha indicates that at normal temperatures it is distinctly crystalline, though having a lattice entirely different from that of frozen rubber. Since the evidence for polymorphism of gutta-percha was so strong, it became of interest to examine the different modifications rontgenographically, and the Debye-Sherrer patterns obtained gave the final confirmation necessary to the theory. Figures 5 and 6 are typical diagrams obtained from the modifications, and 7 and 8 are from the same specimen after stretching.

The appearance of the third strong ring in Fig. 5 is significant of the presence of the α variety, and the intensity of the ring is indicative of the proportion of the α to the β modification. Hauser and Von Susich (*Kautschuk*, 7, 120, 125, 145 (1931)) have, subsequent to the date of British Patent 326,481, published a summary of their experiments on this subject, and their conclusions from the study of their results are in entire agreement with the theory and results already observed. With the assistance of x-ray apparatus specially designed, they have been able to deduce a condition diagram of the hydrocarbon. They have also shown by means of x-ray analysis of strongly orientated specimens, produced by methods somewhat analogous to the racking of rubber, that the identity period of the α form is 8.8 A. U., and that of the β form is 4.9 A. U. For further information the paper should be consulted.

There is a point which they do not seem to have brought out sufficiently strongly in their paper, though they mention it. It is that normal manufactured gutta-percha, that has been heated to temperatures in the neighborhood of 100° C. during the manufacturing process, will exist in the β form almost entirely, although the α modification is the stable variety at ordinary temperatures.

The explanation lies in the fact that the transformation of the β to α modification is very slow on cooling, and the cooling after molding or extruding is relatively rapid.

At normal air temperatures the transformation of the metastable β variety to the stable α variety is so slow that it can be neglected. Samples that have remained unheated for over sixty years have been examined and show practically no signs of transformation to the stable α modification.

Effects on Electrical Properties.—These require considerable explanation and are only of interest in certain special cases. Space will not permit of their being included here, but an outline is given in British Patent 326,481 to which reference should be made.

Practical Methods of Heat-Treatment.—In the manufacture of gutta-percha covered wire for submarine cable core, advantage is taken of the plasticity of the gum, when heated, to extrude it round the copper conductor. This precludes the possi-

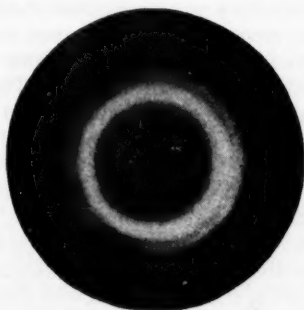


Figure 5

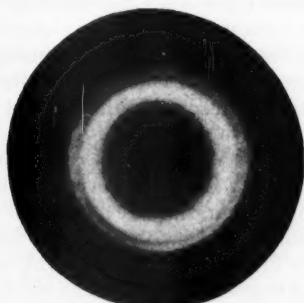


Figure 6

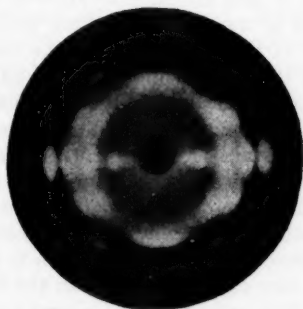


Figure 7

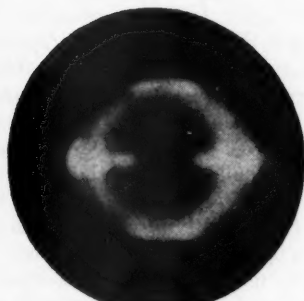


Figure 8

bility of heat-treating material before extrusion, since, as mentioned in an earlier part, the effect of heat-treatment is undone if the gutta-percha is heated above the limiting temperature. These considerations render it essential to be able to carry out the heat-treatment after extrusion, and it would be convenient if this could be done continuously with the extrusion process by passing the covered conductor directly into a bath at a suitable temperature. Unfortunately, the transformation is very slow at temperatures much below the limiting point, and in fact is comparatively slow even if the gutta is maintained accurately at the limiting temperature. When it is remembered that the effect is cancelled by momentary heating to just above the limiting temperature, it will be realized that the accuracy of the control would have to be intense if the process were to be worked at, or just below, this point. Added to these difficulties is the fact that gutta-percha is an excellent heat insulator, and, since the extrusion temperature must be well above the softening

point which it will be remembered is approximately the same as the transformation point, a considerable lag will occur before the temperature of the gutta-percha can drop to that of the bath. This is especially true if the covering is a relatively thick one.

Numerous experiments directed toward this goal were made, but without practical success. Such factors as minimum economical extrusion speeds, and maximum practical tank lengths had to be borne in mind, and it must be remembered that the heating time with a defined speed and tank length cannot be increased by the use of pulleys to pass the core backward and forward in the tank, since the gutta-percha is not hard and set until the treatment is completed.

A peculiar effect was discovered at this time. It was found that the transformation was more rapid when the limiting temperature was approached from a cooler than from a hotter temperature. A special process of heat-treatment based upon this effect has been termed "quenching" and can be utilized to enable the heat-treating process to be made continuous with the extrusion process. The core, as it leaves the extrusion machine, passes as usual into a cooling tank, and this tank is of such a length and kept at a temperature sufficiently low that the gutta-percha when it reaches the end is set to a moderately firm consistency. The time required must obviously vary with the size of the core, the softening point of the gutta-percha, and the temperature both of the water and the extrusion machine. In practice it is found to vary from half a minute up to as much as three minutes. In continuous line with the cooling tank is the treatment tank kept automatically at the desired temperature. It must have a partition wall common with the first tank and the partition is provided with a hole of suitable size through which the core passes. The length of the treatment tank is also arranged to allow of sufficient time and is again dependent upon the speed of travel. In this case the necessary length is also determined by the proximity of the temperature of the tank to the transformation point. For full treatment the time would be inordinately long and, where this is necessary, other methods must be adopted. In many cases, however, a curtailed treatment is sufficient and one to two minutes is often enough for this purpose. The gutta-percha at this stage is not sufficiently hard to be passed over a pulley because the full treatment has not been given. It is necessary therefore to provide a third tank also having a common wall and in line with the second. In this tank the gutta-percha is finally chilled and hardened before being run onto a drum in the usual manner. Consideration has been given to a method in which, by means of pulleys, the covered wire can be carried from the third tank into the second for a further treatment, and this can be repeated several times before winding-off onto a drum. This method is somewhat cumbersome and has several objectionable features, which need not be enlarged upon here.

It has already been said that in those cases in which full treatment is necessary, methods other than the continuous one, just described, must be used. Moreover, it will be appreciated that, since the gutta-percha has already been shaped to the wire, it must not be heated to a temperature at which it will soften, unless it is supported in some manner.

A step-by-step process has been devised by which the treatment can be effected upon a drum without softening the gutta-percha sufficiently to deform it, even when large quantities are placed upon the drum. This process is similar to that of the heat-treatment of metals below their melting points, but the analogy does not carry very far. It depends upon the early observation that the phenomena is progressive with temperature providing, of course, that the "limit" is not exceeded.

The effect of the amount of resin upon the limiting temperature of a specimen of gutta-percha has been shown to be largely confined to the solvent power of the

resin upon the hydrocarbon. As a consequence it is necessary to devise a different schedule of heating times and temperatures for every different type or mixture of types of gums. It will be sufficient here, however, briefly to refer to a normal mixture such as is used for submarine cable insulation, and having a softening point of about 55°C . Sufficient allowance has been made in the schedule given for the heat to diffuse through the drum containing three miles of core insulated with the gutta-percha. The drum can be placed in a tank of water at 38°C . heated as follows: 3 hours at 38°C ., 43°C ., 46°C ., 48°C ., and 49°C .; 4 hours at 50°C ., and 5 hours at 51°C . Provision should be made for agitating the water, and the temperatures should be maintained constant to within 1°C . at the first temperatures, and to within $\frac{1}{4}^{\circ}\text{C}$. at the final temperatures. If preferred the temperature may be varied continuously so as to follow a time curve which can be obtained by plotting the above figures on squared paper.

Special apparatus has been devised for carrying out this process and particulars can be obtained by reference to the patent already cited.

Summary

The hydrocarbon from balata or gutta-percha is polymorphic, and the modification in which it is usually known is the metastable variety, but it can be converted to the stable modification by one of a variety of comparatively simple heat-treatments. The α modification, to which it is converted by the heat-treatment, has somewhat different properties and these are compared. Some beneficial effects are reported which enable gutta-percha products to become the basis of a very superior variety of submarine cable insulation, which has been called K.-gutta.

In writing this article the author is indebted to W. S. Smith and H. J. Garnett for criticism and advice and to F. Mattingley and H. F. Wilson and others of the laboratory staff for assistance and coöperation in carrying out this work. Thanks are also due to the Telegraph Construction and Maintenance Co., Ltd., for permission to publish these results.

Modifications of the Gutta-Percha Hydrocarbon. II

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The Spongy Product

In the experiment previously reported¹ in which agitation was carried out, it was found that the spongy product had changed after one and one-half to two hours, in that most of the portion which had been soluble in benzene had precipitated out. Accordingly the spongy product may have contained a metastable modification of the hydrocarbon which is soluble in benzene below 19°, so that the stable modification which is only slightly soluble in the solvent at this temperature is precipitated out.

Moreover, the change which was observed in the solubility of the spongy product after pressing might be attributed to a similar transformation into the stable modification.

Since it is not improbable that these changes were accompanied by a diminution of the volume, a few experiments with the dilatometer were carried out in the way described below.

Experiments with the Dilatometer

A quantity of the product was placed in a round flask of about 50-cc. capacity or in a wide glass tube in such a way that compression of the product was avoided as much as possible. Separate pieces were used by preference, others were cut with scissors. A capillary tube was fused into the flask or the glass tube. The dilatometer assembled in this way was filled with water in the usual way by means of a pipette and an air pump. Air was removed from the water and from the spongy product by means of a water-jet vacuum pump at ordinary temperature. In this operation, whereby air was forced through the water in the pipette, the raising to a higher point and subsequent dropping of the flask or of the tube to a point lower than the pipette accelerated this phenomenon considerably. The experiment was terminated when a bubble, formed in the flask after raising the latter, disappeared completely or left only a trace on shutting off the pump.

The spongy product was prepared from sheet balata with petroleum ether (b. p. 50-80°) and was washed with this solvent, but not recrystallized. Diagram 1 shows the result of this experiment.

Upon heating, curve 1 was obtained. At first the product dilated progressively up to 49°, at which point the dilation began to diminish, and at 55° it changed to strong contraction. This continued up to 63°. At this point a rapid dilation began, which at 66° became slower. After cooling, the surface of the liquid in the neck of the flask had become lower, and on heating again it reached the zero mark only at 58°.

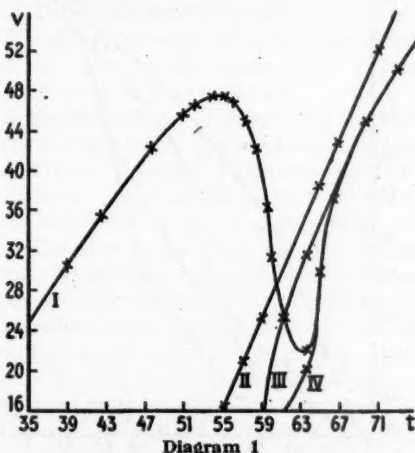
The dilatometer was then heated to 80° and the cooling curve 2 was obtained. The contraction was regular and the whole curve shows, as far as it could be drawn, the condition of the liquid since, as is shown in the following dilatometer experiment, crystallization takes place only at 45°, and it is manifest by a stronger contraction. It is to be noted that the first part of curve 1 is higher than curve 2.

¹ Cf. *Rec. Trav. chim.*, 51, 63 (1932); *RUBBER CHEMISTRY AND TECHNOLOGY* 5, 287 (1932).

The dilatometer was then heated to approximately 90° , and the flask maintained at this temperature for 1 hour. It was then placed in melting ice and rapidly cooled by moving it about in order to change the hydrocarbon into the β -modification. This was repeated twice more. In the other experiments with the dilatometer, the heating and placing in ice were repeated until the surface of the liquid no longer showed any change at ordinary temperature. Heating gave β -curve 3.

The flask was then heated to 60° and allowed to cool slowly in warm water. This was also repeated two more times. In other experiments with the dilatometer, the heating and slow cooling were repeated until a change was no longer to be seen in the liquid at ordinary temperature. On heating, α -curve 4 was obtained. This curve coincided with curve 1 from 64° on, which shows that the spongy product contains the α -modification, as Katz has already demonstrated by x-rays. Furthermore the curves show that the β -modification has a greater volume than the α -form and that both assume a larger volume on fusion.

The dilatometer was weighed and water was added until the surface of the liquid



stood at 2.6 at 11° , showing an increase of 1.1 g. in weight. The level of the surface of the liquid at the beginning of the experiment was 7.1 at 10° .

When the dilatometer was opened, it was found that it contained 8.341 grams of hydrocarbon and 62.239 grams of water. Since 7.18 centimeters of the capillary tube had a content of 1.5 cc. (obtained by removal of the water contained in it) the contraction at 11° was approximately 1.2 cc., and for 10 grams of hydrocarbon was therefore approx. 1.4 centimeters.

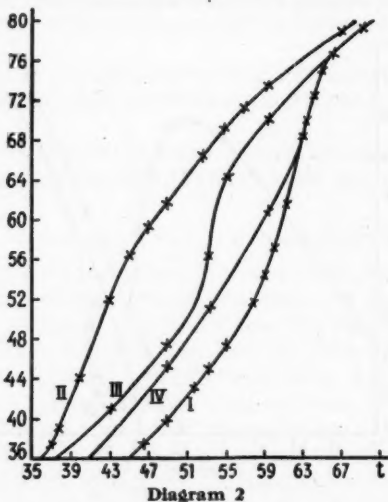
An experiment with the dilatometer was carried out with another portion of the spongy product after it had first been ground up in a mortar into a large number of small pieces. Diagram 2 gives the results of this experiment.

Curve 1, obtained by heating at the beginning of the experiment, shows no contraction and is situated below the other three curves. The fusion range was $58-66^{\circ}$. Cooling curve 2 shows the beginning of crystallization at 45° which takes place under contraction. β -curve 3 has its fusion range from 49° to 59° , and α -curve 4 has a fusion range from 59° to 66° .

At first the surface of the liquid was 14.9 at 14° , after fusion and transformation into the β -modification it was 20.1 at the same temperature, and when the hydrocarbon contained the α -modification it was 18.1.

When the dilatometer was opened it was found that it contained 64.51 grams of water and 7.48 grams of hydrocarbon. Since 66.5 centimeters of the capillary tube had a capacity of 2.1 cc., the difference in volume between the original product and the α -modification, obtained from this by fusion, was 3.2 centimeters or 0.1 cc. at 14°, *i. e.*, 0.13 cc. per 10 grams of hydrocarbon. The difference in volume between the α - and β -modifications at the same temperature reached 2 centimeters, or 0.063 cc., *i. e.*, 0.09 cc. per 10 grams of hydrocarbon.

A dilatometer experiment was also carried out with a product previously fused in water and crystallized from petroleum ether. The spongy product contracted between 54° and 61° and expanded from 61° to 67°. After fusion it began to crystallize at 39°. The fusion range of the α -modification was from 57° to 66°, that of the β -modification from 50° to 57°. In the beginning the level of the liquid was 12 at 15.5°; when the hydrocarbon contained the α -modification it was -2 and when the β -modification was present it was 0.2 at the same temperature.



When the dilatometer was opened it was found that it contained 61.3 grams of water and 5.476 grams of hydrocarbon; 83.2 centimeters of the capillary tube had a capacity of 2.8 cc. It was calculated from these data that the contraction was 0.9 cc. per 10 grams of hydrocarbon, the difference in volume between the α - and β -modifications was 0.13 cc.

Following this an experiment was carried out with the dilatometer with a hydrocarbon which, after it was crystallized from benzene in an ice-box, had stood for two days in the laboratory at ordinary temperature in the benzene. The curves obtained show a great similarity to those obtained from the small pieces. No contraction is to be seen in curve 1, and this lies below the other three curves. The fused hydrocarbon began to crystallize at 42°. The fusion range was from 61° to 69° at first, that of the α -modification from 60° to 68° and that of the β -modification from 51° to 57°.

On opening the dilatometer, 69.5 grams of water and 4.08 grams of hydrocarbon were found. Since 65.8 centimeters of the capillary tube had a capacity of 3.5 cc. and the level of the surface of the liquid in the beginning and when the hydrocarbon contained the α -modification was 2.3 and 3.2 centimeters, respectively, at 12.5°,

the difference in volume was 0.048 cc. for 4.08 grams of hydrocarbon, or 0.12 cc. per 10 grams. The difference in volume between the α - and β -modifications was 0.8 centimeters or 0.041 cc. at 12.5°, *i. e.*, 0.1 cubic centimeter per 10 grams of hydrocarbon.

Since the contraction of the spongy product may depend upon impurities, a pure product was prepared in the way described below.

Purification of the Hydrocarbon with Benzene

Sheet balata, cut up into pieces, was heated with petroleum ether (b. p. 50–80°), with agitation, until the strips had dissolved. A little water was then added, and it was agitated vigorously, after which, upon standing in warm water, the previously milky solution deposited a brown precipitate and became clear. The solution was filtered and allowed to crystallize in an ice-box. The spongy product obtained was removed under slight compression and was washed with petroleum ether. After having stood in the air for 24 hours in darkness in order to free it from petroleum ether, it was dissolved in benzene and the resulting solution was allowed to crystallize in an ice-box. It was then let stand 24 hours in the laboratory at 15° to 18°, and the crystalline mass was removed and washed with benzene. The product was recrystallized twice more from benzene in the same manner. It was then dispersed in benzene and left in the laboratory. The next day it was again removed and put in fresh benzene. On the day before it was to be used, a part of it was removed, was washed with benzene and let stand 24 hours exposed to the air in darkness in order to free it from benzene. This method of purification was so controlled that the benzene filtrate, from which 20.6 grams of pure product were obtained, was distilled, the residue was dissolved in petroleum ether, and these solutions were placed in the ice-box. After crystallization these solutions were poured off from the crystals or filtered if necessary, then distilled off, and both the residue and the crystals were weighed. The yields of resin in a half liter of filtrate for the three crystallizations were 1.7 grams, 0.28 gram, and 0.016 gram; the yields of crystals were 0.25 gram, 0.52 gram, and 0.17 gram. After standing 24 hours in the laboratory, the benzene solution contained only 6 milligrams of resin and 8 milligrams of crystals in one-half liter. The product purified in this way was therefore practically free from resins.

Dilatometer Experiments with the Purified Product

A quantity of this product (8 grams) was dissolved in petroleum ether (b. p. 50–80°) (400 grams) and the product obtained by crystallization at ordinary temperature was removed. After it had stood in air in darkness for 24 hours it was ready for use. In place of water the dilatometer was filled with an alkaline hydroquinone solution to avoid the possibility of any adhering oxygen being held by the finely divided material. The crystallized product was very easily oxidized; 5.2 grams heated in the sealed tube at 63° for two and one-half hours absorbed 6.6 cc. of oxygen, since the tube when opened under water took up this quantity of water. Care was taken in sealing the tube that it was first exhausted and then the narrow part was sealed after cooling in order to cause as little change in temperature by heating as possible. Even at ordinary temperatures in darkness the product absorbed oxygen, and 9.5 cc. were consumed in 8 days. If, therefore, oxygen had been retained by the finely divided substance, upon heating contraction should result from oxidation of the hydrocarbon.

The curve obtained with this dilatometer shows a contraction between 61° and 64.5°, and an expansion from 64.5° to 67°. At the beginning the level of the liquid was 10.8 at 13°, and after fusion and transformation of the substance to the α -

modification, the level dropped to 5.5 at the same temperature. Therefore the contraction at 13° was 5.3 centimeters, or 0.32 cc., since 68.7 centimeters of the capillary tube contained 4.1 cc. Since the dilatometer contained 3.5 grams of hydrocarbon, the contraction was 0.9 cc. per 10 grams of hydrocarbon. The fusion range of the α -modification was 61° to 67°, that of the β -modification 51° to 57°. The difference in volume between 10 grams of the hydrocarbon in the α - and β -modifications was 0.11 cc.

Eight grams of the purified product were dissolved in 400 cc. of petroleum ether (b. p. 50–80°) in which a little *p*-toluidine was dissolved as an antioxidant. The dilatometer was also filled with an alkaline hydroquinone solution. The result was very similar to that of the previous experiment. Contraction also occurred between 61° and 64.5°, and expansion between 64.5° and 67°. In the beginning the level of the liquid was 11.6 at 13.5°, and after fusion and transformation into the α -modification it was 2 for the same temperature. Accordingly the contraction at 13.5° was 9.1 centimeters, or 0.54 cc., since 68.7 centimeters of the capillary tube contained 4.1 cc. Since the dilatometer contained 3.717 grams of hydrocarbon, the contraction was 1.45 cc. per 10 grams. The fusion ranges of the α - and β -modifications were likewise 61° to 67° and 51° to 57°. The dilatometer was opened and the hydrocarbon, fused in water with hydroquinone, was compressed and cut into strips. The fusion range of the α -modification was 60° to 66° in the dilatometer.

Hauser and von Susich (cf. *Kautschuk*, 7, 125 (1931)) found by x-ray analysis that the fusion points for the α - and β -modifications were 64° to 66° and 55° to 57°, respectively, which naturally cannot agree with the fusion ranges, since only the end of the fusion is determined roentgenographically, i. e., the point at which the substance no longer gives an α - or β -diagram. The agreement is therefore satisfactory.

Contraction

From the results of the last two dilatometer experiments, calculations were made to determine how great the expansion would have been if no contraction had taken place. The contraction in the first experiment was within 3.5°, and since the extension during the previous 4 degrees from 57° to 61° was 3.2 centimeters, the contraction would have to be 3.2 centimeters within 3.5°. However, it amounted to only 0.2 centimeter between 61° and 64.5°. Therefore, if during the contraction there had been no elongation and the substance had not shrunk during fusion from 64.5° to 70°, there would then have been less than 3 centimeters contraction after cooling. However the value found was 5.3 centimeters.

In the second experiments the result was similar; the calculation gave 2 centimeters, and after cooling a contraction of 4.5 centimeters was found.

In order to ascertain whether this difference was caused by extension during contraction from 61° to 64.5° or whether it was caused by contraction during fusion from 64.5° to 67°, a pycnometer was used. The pycnometer with a round base contained 25.620 grams of water at 15°. 2.401 grams of the spongy product were weighed, water was added, and air was passed through at ordinary temperature with a vacuum pump. At 15° it contained only 22.791 grams of water. After heating to 64.5° it contained 23.146 grams of water at 15°. After fusion and heating to 80°, it contained 23.122 grams of water at 15°, and after transformation to the α -modification, 23.148 grams. There was no contraction during fusion from 64.5° to 67°, therefore contraction during fusion from 61° to 64.5° was not accompanied by extension. The substance fused while contraction took place. From this experiment, the calculated specific gravity at 15° was 0.841 for the spongy prod-

uct, and after heating to 64.5° it was 0.961; likewise it was 0.961 for the α -modification and 0.951 for the β -modification.

At 15° the volume of 10 grams of the α -modification was 10.406 cc. and of the β -modification 10.515 cc., *i. e.*, a difference of 0.109 cc. The experiments with the dilatometer gave for these differences 0.09, 0.13, 0.10, 0.11 cc., or an average of 0.0107 cc.

The volume of 10 grams of the spongy substance at 15° was 11.891 cc., and there was therefore a difference of 1.485 cc. between this and the α -modification. The dilatometer experiments gave for these differences: 1.4, 0.9, 0.9, and 1.45 cc., or an average of 1.15 cc.

In the next communication these results will be discussed.

Summary

It was proved by dilatometer experiments that the spongy product contracts between 61° and 64.5° , and that this contraction is not caused by an impurity or by oxidation. An experiment using a pycnometer showed that contraction was accompanied by fusion, and that during fusion with tension at 64.5° to 67° no contraction took place.

The products obtained by grinding the spongy product in a mortar and by crystallizing it from a benzene solution in an ice-box showed no contraction; on the contrary after fusion they showed a slight expansion at ordinary temperature.

A method is given for obtaining a pure hydrocarbon from sheet balata.

The Refractometry of Rubber and Gutta-Percha Hydrocarbons

I. The Influence of Depolymerization and Oxidation on the Refractive Exponents of These Hydrocarbons

F. Kirchhof

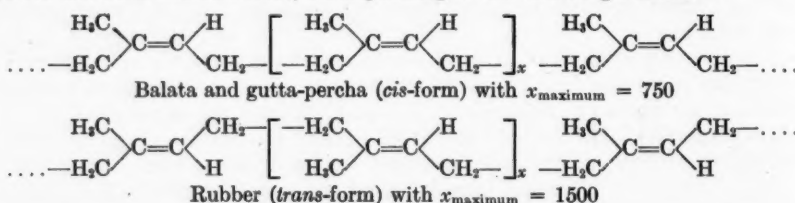
HAMBURG

The refractive indices of rubber and of gutta-percha have been measured repeatedly, and yet no particular significance seems to have been attached to them up to now. Apparently it has been satisfactory merely to show that rubber and gutta-percha show practically the same refractive index. The following table is a summary of the values known to the author.¹

TABLE I
SOME VALUES FOR n_D AND M_D OF RUBBER AND GUTTA-PERCHA WHICH HAVE BEEN FOUND PREVIOUSLY

Substance	Temperature, °C.	Refractive Index, n_D	Molecular Refraction, M_D	Investigator
Rubber	20	1.5219	22.46	A. D. Macallam and G. S. Whitby
Rubber	16	1.5222	22.57	E. Geiger
Gutta-percha	15	1.5250	...	D. F. Twiss
Gutta-percha	20	1.5230	...	(Calculated 20°)

According to experiments by Staudinger² in particular, there are differences in the molecular size of balata on the one hand and rubber and gutta-percha on the other, and also differences in the type of chain formation of their isopentene groups. According to Staudinger, both gutta-percha and balata represent the *cis*-form and rubber the *trans*-isomeric form, corresponding to the following scheme.



Since both the molecular size and stereoisomerism³ have a distinct influence on the index of refraction, differences between the rubber and gutta-percha hydrocarbons dependent upon these factors are not unexpected. This is based on the assumption that degrees of polymerization of hydrocarbons of the same molecular size and of the same purity are compared with one another. To settle this problem a number of questions must first of all be answered.

The object of the present investigation was to determine to what extent the natural impurities (extraneous substances), as well as depolymerization and oxidation, influence the index of refraction of the rubber and gutta-percha hydrocarbons.

Experimental

The following measurements were carried out with the easily heated Zeiss-Abbé refractometer (Model 1). The raw rubber and the gutta-percha were placed in the

form of thin sheets or chips between the halves of the prism of the refractometer. The prisms were closed and were warmed to 70° by means of a heating device. After clamping the halves of the prisms together, which flattened the softened sheets within into films about 0.2 mm. thick, readings were begun. While cooling, which was at the rate of 1° C. per minute, the readings were taken every 5° and then every 10°. The final readings, which were ordinarily taken at 20° C., were in many cases checked after several hours. Only slight deviations were found from the initial readings, *viz.*, up to two places in the fourth decimal of the index of refraction.

A. Influence of the Origin as Well as of the Acetone-Soluble and Benzene-Soluble Components upon the Indices of Refraction of Various Kinds of Raw Rubber

First of all an investigation was made to determine to what extent the indices of refraction of various kinds of rubber differ and to what degree the non-rubber components of the individual rubbers influence the index of refraction of their hydrocarbons. More specifically the influence of easily removable acetone-soluble non-rubber components, the greater part of which are incorrectly called rubber "resins," were studied.

Table II shows the index of refraction of a number of types of raw rubber before and after 8 hours' extraction with acetone.

TABLE II

THE INDICES OF REFRACTION OF DIFFERENT TYPES OF RAW RUBBER BEFORE AND AFTER EXTRACTION WITH BOILING ACETONE FOR 8 HOURS

Temp., ° C.	Ceylon Crepe Ia		Ceylon Crepe IIIa		Smoked Sheet		Para Extra Fine		Black Congo	
	Be- fore ^a	After ^c	Be- fore ^a	After ^c	Be- fore ^a	After ^c	Be- fore ^b	After ^c	Be- fore ^b	After ^c
60	1.5058	1.5060	1.5058	1.5068	1.5060	1.5075	1.5070	1.5085	1.5080	1.5075
55	1.5068	1.5070	1.5075	1.5090	1.5090	1.5085	1.5100	1.5100	1.5095
50	1.5100	1.5090	1.5110	1.5085	1.5110	1.5105	1.5120	1.5125	1.5110
45	1.5125	1.5115	1.5120	1.5142	1.5100	1.5120	1.5122	1.5140	1.5140	1.5130
40	1.5140	1.5135	1.5138	1.5155	1.5120	1.5150	1.5160	1.5162	1.5158
30	1.5188	1.5190	1.5180	1.5192	1.5155	1.5195	1.5180	1.5200	1.5183	1.5180
25	1.5200	1.5200	1.5182	1.5213	1.5205	1.5195
20	1.5218	1.5218	1.5218	1.5235	1.5195	1.5215	1.5220	1.5238	1.5242	1.5235

^a The sheet was taken from the original sample.

^b The sheet was rolled out thin just before the extraction.

^c The acetone-extracted sheets were dried at 80° C. to constant weight.

The figures show clearly that the *Hevea* rubbers generally have a higher index of refraction after acetone extraction than in the crude state, whereas African Congo rubber shows just the opposite effect. The difference in the n_D values amounts to about two points of the third decimal. The reason for the apparent exception in the behavior of Ceylon crepe will be referred to later. Doubtless it is to be attributed to the great sensitivity to heat and oxidation of this very pure plantation rubber.

If the observations above are correct, *Hevea* rubber "resins," which are composed predominantly of fatty acids, must have a lower index of refraction, and the resins of African rubber on the contrary a higher index of refraction than their respective hydrocarbons, since as is known indices of refraction are additive. The values in Table III show that this is true without an exception.

The resins of African types of rubber (preponderantly the *Landolphia* type) differ appreciably with regard to their index of refraction from those of *Hevea* rubber, just as they do polarimetrically.⁴

In so far as the differences in the indices of refraction of the acetone-extracted

types of rubber are concerned, they may be ascribed chiefly to differing "polymerizations" or "degrees of aggregation" (depending upon whether the molecular or micellar theory of rubber is accepted), whereas the acetone-insoluble non-rubber components (proteins, oxidation products, and coloring substances) appear to play only a secondary part. Thus in the extracted state at 20° C., pale Ceylon crepe Ia and highly smoked sheet had practically the same index of refraction. The same was true of pale crepe IIIa and light brown Para rubber. Moreover, according to Pummerer, latex rubber freed from protein substances and resins by purification has almost the same index of refraction as Ceylon crepe (see Table VII).

TABLE III
INDICES OF REFRACTION OF ACETONE-SOLUBLE EXTRACTED SUBSTANCES (RUBBER RESINS) OF DIFFERENT TYPES OF RAW RUBBERS

Temp., ° C.	Designation of Type of Rubber from Which Extract Was Obtained	n_D^a
22	Ceylon crepe Ia	1.4920
60	Ceylon crepe Ia	1.4780 ^b
22	Ceylon crepe IIIa	1.4980
21.5	Smoked sheets	1.5020
22	Para extra fine	1.5085
22	Congo black	1.5283

^a Before measuring the extracts were dried one hour at 100° C. and a short time at 120° C. and were tested until the refractive index was constant.

^b According to Rindstalg n_D at 60° C. = 1.4510, that of pure stearic acid = 1.4340.

It should not be forgotten that changes may result from the acetone extraction and subsequent drying by heat which, in the case of very sensitive Ceylon crepe Ia, may lead to compensations in that the increase in the index of refraction brought about by the extraction is nullified by a decrease resulting from depolymerization. This will be reported in greater detail in the following section.

It was then of interest to determine to what extent the sol and gel parts of the rubbers differ refractometrically. For this purpose, the portions of the benzene solutions which deposited after standing 1 year in darkness were used after being washed three times with benzene and decanted off. The benzene-soluble portion of sulfo-cyclorubber (sulfuric acid Congo rubber) was studied refractometrically in order to determine the influence of cyclicization on the index of refraction.

Table IV gives a summary of the results obtained.

TABLE IV
INDEX OF REFRACTION OF SOL, GEL, AND CYCLO RUBBERS

Temp., ° C.	Ceylon Rubber	Crepe IIIa Gel Rubber	Congo Rubber Sol Rubber	Rubber Gel Rubber	Congo-cyclo- Rubber (Benzene-soluble Portion)
60	1.5070	1.5065	1.5078
55	1.5085
50	1.5105	1.5100	1.5125
45	1.5120	1.5130	1.5130	1.5133
40	1.5142	1.5145	1.5140	1.5150
30	1.5182	1.5190	1.5185	1.5192	1.5288
20	1.5222	1.5225	1.5228	1.5235	1.5320

The gel portions of both the *Hevea* and the Congo rubbers show noticeably higher indices of refraction than the corresponding sol portions. To what extent this higher light refraction depends upon the impurities (protein substances, oxidation products, coloring substances), and to what extent upon higher degrees of polymerization, remains unsettled for the present. Furthermore, it is evident from Table IV that the light refractive power of the sol portions of the rubbers from

widely different origins exhibits definitely smaller differences. This favors the idea of a greater influence of the benzene-insoluble non-rubber substances.

B. Influence of Mastication on the Index of Refraction of Raw Rubber

If the molecular size of rubber influences its index of refraction, then this index would have to change appreciably during mastication.

That rubber in solution is extraordinarily sensitive to oxygen has been shown many times (Staudinger, *loc. cit.*). Quite a similar influence of atmospheric oxygen during the mastication of raw rubber has recently been established, and it has also been shown to be the cause of the rubber becoming plastic.⁵

According to Staudinger this absorption of oxygen does not involve addition at the so-called double bonds, but is an intermediate transposition which leads to a spitting up of the long fiber molecules and therefore to a form of cracking.

Likewise as would be anticipated, rubber and gutta-percha are fundamentally different during mastication and depolymerization by heat in so far as changes in their indices of refraction are concerned. The index of refraction of raw rubber decreases at the beginning and only begins to increase at the time when there is a perceptible addition of oxygen, whereas the index of refraction of gutta-percha increases steadily upon standing in air. In the case of rubber the first step involves a considerable diminution in plasticity (viscosity), whereas gutta-percha shows no such phenomenon.

Gutta-percha (in the following experiments pure crystallized Tjipetyr gutta-percha was used) becomes brittle and is transformed into bright yellow, partially resinous, acetone-soluble oxidation products which differ distinctly from those of rubber, at least in the initial phase of the oxidation.

Table V gives a summary of the changes in the index of refraction of Ceylon crepe Ia for different times of mastication. Since, as was shown in the previous section, acetone extraction leaves the index of refraction of this rubber practically unchanged, the untreated raw substance was used.

TABLE V
INFLUENCE OF MASTICATION ON THE INDEX OF REFRACTION n_D OF CEYLON CREPE Ia

Temp., ° C.	Kind of Preliminary Treatment of the Raw Rubber		
	(a) Unmasticated n_D	(b) 1 Hr. Hot Mastication Stored for 1 Yr. in Darkness, n_D	(c) 4 Hrs. Hot Mastication Stored for 6 Weeks n_D
70	1.5028*	1.5008
65	1.5050	1.5026
60	1.5070	1.5060	1.5045
55	1.5090	1.5080	1.5068
50	1.5120 (49°)	1.5100	1.5088
45	1.5135	1.5120	1.5106
40	1.5150	1.5140	1.5126
35	1.5170 (36°)	(33.5°) 1.5155
30	1.5196 (29.5°)	1.5180	1.5168
25	1.5210	1.5200	1.5185
20	1.5226*	1.5220	1.5210

* The values were practically the same when read again two hours later.

Both Table V and Figure 1 show that there was a distinct decrease in the index of refraction with progressively increasing periods of mastication, which amounted to about 3 units at the higher temperatures observed and to about 2 units of the third decimal at the lower temperatures during milling for 4 hours and subsequent standing in darkness for 6 weeks at about 10° C. (the 5 kg. crepe block was "frozen")

after this time so that it became partially crystallized). As can be seen, the decrease in the index of refraction brought about by mastication is a permanent effect, whereas the plasticity of masticated rubber reverts to its original value or may even reach a lower one.

It is also clear that these facts may have a practical application, since they make possible a very rapid and economical test of both the uniformity and purity of the raw material, and also make it possible to follow its behavior during mastication and storage.

C. Influence of Depolymerization by Heat on the Index of Refraction of Rubber and Gutta-Percha

Like mastication, heating strongly in air causes a more or less pronounced decrease in the refractive index of raw rubber. Depending upon their origin, previous history, and purity, the various types of rubbers show a differing sensitivity under

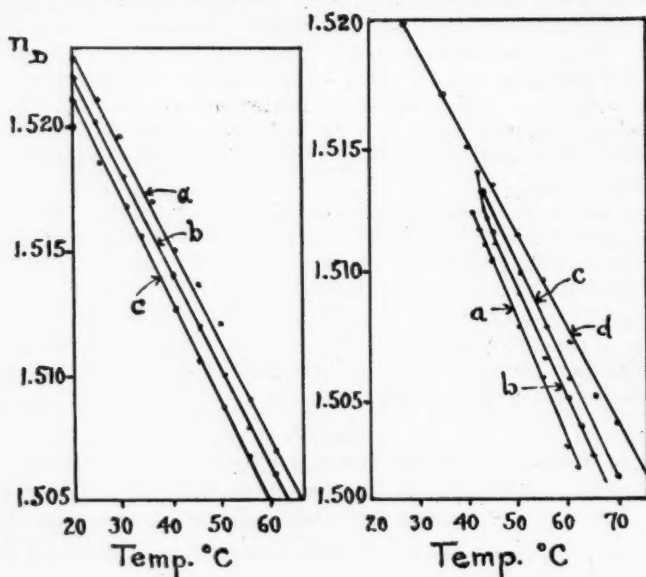


Figure 1

Figure 2

the same heat treatment, which is also manifest superficially by varying degrees of tackiness from a mere softening to a condition of almost fusion. There is almost no doubt that, as in mastication, these physical changes resulting from depolymerization by heat depend upon a trace of oxidation which brings about "cracking" of the long fiber molecules. Table VI shows the influence of depolymerization by heat on the refractive index of different kinds of rubber. This table shows that the unmasticated latex film shows a distinctly higher index of refraction than the sol rubber of Ceylon crepe prepared by evaporation of a benzene solution, even after three times as long a heat treatment as the latter. The sol portion of Congo rubber shows, on the contrary, the same light refraction as the unmasticated latex rubber, as in Table II. The decrease in the light refraction after the same heat treatment is, however, greater with Congo rubber than with latex rubber. This difference is apparently attributable to the greater sensitivity of African rubber toward heat and depolymerization agents. Likewise African rubbers be-

have somewhat differently under ozonization (Harries) or treatment with concentrated sulfuric acid (Kirchhof) from Para rubber and other types of *Hevea* rubber.

TABLE VI

"Latex" Rubber Unmasticated ^a		Ceylon Crepe Benzene-soluble Portion ^b		Congo Rubber Benzene-soluble Portion ^b	
Before Heated 3 Hrs. at 120° C.	After ^c Heated 1 Hr. at 120° C.	Before Heated 1 Hr. at 120° C.	After ^d Heated 1 Hr. at 120° C.	Before Heated 1 Hr. at 120° C.	After ^e Heated 1 Hr. at 120° C.
1.5055	1.5045	1.5085	1.5050
1.5072	1.5062	1.5070	1.5072
1.5108	1.5100	1.5105	1.5092	1.5115
1.5132	1.5125 (44°)	1.5120	1.5117	1.5130
1.5155	1.5142	1.5140	1.5155	1.5150
1.5170	1.5162	1.5162	1.5160	1.5170
1.5190	1.5183	1.5182	1.5180	1.5190	1.5180
1.5232	1.5225	1.5222	1.5218	1.5232	1.5218

^a Obtained by evaporation from the latex.

^b After storage for about 1 year in darkness the benzene soluble portion had separated from the completely clear solution. It amounted to approximately 50 per cent, i. e., 20 per cent of the original total rubber concentration of the solution.

^c The rubber film was not softened and the outer surface was only slightly sticky.

^d The rubber film was partially softened and the outer surface was distinctly sticky.

^e The rubber film was entirely melted and had become very sticky.

In contrast to the rubber hydrocarbons, the most highly purified and crystallized Tjipetyr gutta-percha shows no decrease in the refractive index when warmed in air, but rather a steady increase.

Among the more evident changes are a lowering of the freezing point (the appearance of turbidity upon cooling after fusion), yellowing, and after a longer time an empyreumatic odor, which is distinctly different from the odor of the levulinic aldehyde of oxidized rubber.

The purest unmilled Tjipetyr gutta-percha shows at 45° an index of refraction which is about two points in the third decimal place lower than that of Ceylon crepe. Until further data is obtained, this difference may be ascribed to the lower degree of polymerization of this hydrocarbon.

The refractometric behavior of crystallized gutta-percha upon repeated warming to 70° C. and subsequent cooling leads to certain conclusions. As Hauser and v. Susich⁶ found, gutta-percha consists of two modifications (α - and β -gutta-percha) which are distinctly different from one another in their melting points and x-ray diagrams. The great increase in the index of refraction, after the sharp line of separation in the refractometer becomes indistinct, likewise indicated the presence of different modifications⁷ (see also Fig. 2).

Since the gutta-percha in the foregoing experiments was heated above the transformation point (68° C.), according to v. Susich the β -modification forms upon solidifying, because this is stable at 68°. The indices of refraction given above correspond therefore to the solidification point (40° to 42° C.) of the β -modification. Below this latter temperature the α -modification with its higher index of refraction seems to be formed again in increased proportions. The continuous increase in the value of the refractive index upon repeated fusion and solidification, as well as upon standing in the air, is, however, to be attributed to oxidation. In distinction to rubber, this also appears to take place at the "double bonds," with the formation of more highly refractive oxidation products, whereas with rubber a degradation into short molecules predominates at first, with a resulting decrease in the index of refraction. Gutta-percha behaves therefore like linseed oil when it is blown, or when it forms linoxyn, which is likewise accompanied by an increase in the

refractive exponents. It should be mentioned in the case of rubber as well that after the refractive index has reached a minimum it increases again upon further oxidation, as in the case of gutta-percha.

Table VIII shows the differences just described.

TABLE VII

THE EFFECT OF REPEATED FUSION AND COOLING AND ALSO PROLONGED OXIDATION IN AIR UPON THE INDEX OF REFRACTION OF PUREST TJIPETYR-GUTTA-PERCHA

Temp., ° C.	(a) Purest Tjipetyr- Gutta- Percha	(b) 1 Hour after Measure- ment ^a	(c) 24 Hours after Measure- ment ^a	(d) 72 Hours after Measure- ment ^a	(e) After 2 Years Storage in Air (Oxidized)
70	1.5010	1.5015	1.5020	1.5040
65	1.5012	1.5015	1.5028	1.5038	1.5050
60	1.5032	1.5035	1.5050	1.5058	1.5072
55	1.5058	1.5060	1.5065	1.5080	1.5096
50	1.5075	1.5080	1.5090	1.5100	1.5115
45	1.5105	1.5108	1.5110	1.5116	1.5135
44	1.5110 ^a	1.5120
43	1.5115
42	1.5180	1.5125 ^a	1.5140 ^a	1.5130 (42.5°)
40	1.5215 ^b	1.5330 ^b	1.5140 ^a	1.5155
35	1.5215 ^b (37°)
30	1.5170
25	1.5210 (26°)
20	1.5230

^a Beginning of indistinctness in the line of separation in the refractometer.

^b Complete indistinctness of the line of separation as a result of recrystallization.

TABLE VIII

REFRACTOMETRIC BEHAVIOR OF LINSEED OIL, GUTTA-PERCHA AND RUBBER UPON OXIDATION IN THE AIR

Condition of the Substance	Linseed Oil		Purest Tjipetyr- Gutta-Percha	Hevea Rubber Purified Accord- ing to Pummerer
	d_{20}	$n_D^{22.5}$	n_D^{20}	n_D^{20}
Untreated	0.930	1.4790	1.5105	1.5220
Oxidized	0.960	1.4858	1.5230	1.5125 ^b
Oxidized	Linoxyn	1.4920	1.5265 ^a	1.5145 ^c

^a Acetone-insoluble residue of oxidized gutta-percha.

^b After 144 hours' oxidation of the highly depolymerized product^b in air.

D. The Relation between the Index of Refraction and the Viscosity

According to Staudinger (*loc. cit.*) there is a definite relation between the molecular size of the rubber and gutta-percha hydrocarbons and the viscosity of their dilute solutions. Since the molecular size of rubber has a noticeable influence on its index of refraction, a similar relation must also exist between its index of refraction and the viscosity of its solutions. To this end, a study was made of the influence of depolymerization by heat on both the viscosity of benzene solutions of rubber and on the index of refraction of the rubber films obtained from these solutions. Solutions of approximately 2 per cent were tested in an Ostwald viscosimeter, then refluxed 3 hours on an oil bath to around 80° C., and were measured after making up to the original concentration. Rubber films from the corresponding solutions were examined in the refractometer at 20° and 45° C.

In these experiments it was repeatedly observed that part of the sol rubber solutions after several hours' heating on an oil bath were deposited in a gelatinous form on the walls of the vessel. A polymerization phenomenon is obviously taking place in this process, probably under the action of small quantities of oxygen (formation

of gel rubber according to Staudinger). Likewise the polymerized portions (after evaporation of the solvent) have a noticeably higher index of refraction than those in solution.

Table IX gives the values obtained in these experiments.

TABLE IX
INFLUENCE OF DEPOLYMERIZATION BY HEAT OF RAW RUBBER IN SOLUTION ON THE VISCOSITY AND THE REFRACTIVE INDEX

Types of Rubber and Method of Treatment	Concentration of Rubber Hydrocarbon in the Benzene Solution (Sol Rubber), Volume in %	Viscosity of the Solutions in an Ostwald Viscosimeter at 20° C.		Refractive Index of Solid Rubber Obtained from Solutions	
		Sec.	Relative Viscosity	20° C.	at 45° C.
Ceylon crepe	1.84	2852	203	1.5222	1.5120
Ceylon crepe after 3-hours' depolymerization by heat	1.84	1128	78	1.5219	1.5115
Congo rubber	1.81	666	47	1.5240	1.5143
Congo rubber after 3-hours' depolymerization by heat					
(a) Soluble portion	1.93	550	31	1.5228	1.5130
(b) Difficultly soluble portion	1.93	1.5235	1.5138

These results show certain facts.

There is no simple relation between the relative viscosity of benzene solutions of like concentration of rubbers of different origin and the index of refraction of their solid components. On the contrary, with the same kinds of rubber a decrease in the viscosity is accompanied by a decrease in the index of refraction of the rubber hydrocarbon. In spite of the relatively slight influence of the index of refraction, a relatively great decrease in the viscosity can perhaps be explained (according to the ideas of Staudinger) by the fact that the viscosity is a function of the square of the molecular size, whereas the refractive exponent is only a linear function of the molecular size.

The fundamental difference between the refractometric and viscosimetric behavior of *Hevea* rubber and Congo rubber must depend also, at least in part, upon their constitutions, since Congo rubber is apparently more easily cyclicized than *Hevea* rubber (probably of higher molecular weight). At the same concentrations, cyclo rubbers show lower viscosities than their corresponding pure aliphatic parent substances, but on the other hand they show higher refractive power than the latter because of ring formation (see Table IV).

In conclusion the author might point out the influence of sulfur vulcanization on the index of refraction which, because of the high index of sulfur itself (between 1.9500 and 2.2405), is plainly manifest even with a very small proportion of combined sulfur.⁸

The author wishes to reserve the right to continue this preliminary work, especially with respect to the problem of vulcanization and the oxidation of rubber.

Summary

1. The acetone-extractable substances from different natural rubbers have an appreciable influence on the index of refraction of their hydrocarbons. This influence is different in the case of *Hevea* rubbers from that in the case of African rubbers, for example.

2. The indices of refraction of different kinds of raw rubber after extraction likewise differ appreciably. These differences may be attributed in part to the

different quantities of benzene-insoluble non-rubber substances, in part to differences in the degree of polymerization of the different hydrocarbons.

3. A study of the influence of mastication, depolymerization by heat and oxidation on the magnitude of the light refractive exponents of rubber and gutta-percha shows that there are characteristic differences between the two kinds of hydrocarbons, at least as far as the initial stage of oxidation is concerned.

4. From the purely practical and laboratory-testing points of view, it is possible to detect quickly and easily differences in the same kinds of raw rubber which are originally present or result from mastication, and to follow the course of mastication.

5. Furthermore it appears possible to draw conclusions regarding the constitution of rubber and gutta-percha hydrocarbons from differences in their viscosimetric and osmotic behavior. Accordingly the refractometry of rubber and gutta-percha hydrocarbons may furnish a new way of gaining a deeper insight into the structure of these natural substances.

References

- ¹ "Handbuch der Kautschukwissenschaften," Leipzig, 1930, page 517.
- ² "Concerning the Constitution of Rubber," *Z. angew. Chem.*, **45**, 276, 292 (1932).
- ³ For example, the dimethyl ester of fumaric acid has an index of refraction n_D of 1.4495 at 20° C., and the dimethyl ester of *cis*-isomeric maleic acid an index of 1.4472. *Cis*- and *trans*-isomeric sugars show an analogous behavior.
- ⁴ Hinrichsen and Memmler, "Der Kautschuk und seine Prüfung," page 37.
- ⁵ Cotton, *Trans. Inst. Rubber Ind.*, **6**, 487 (1931); Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).
- ⁶ *Kautschuk*, **7**, 120, 125, 145 (1931).
- ⁷ This disappearance of the sharp line of separation (limiting angle of total reflection) is a convenient means of obtaining an exact estimation of the solidification and fusion points which lie between 5° and 75° C.
- ⁸ A vulcanizate containing about 1 per cent of combined sulfur showed an index of refraction of 1.5450.

The Determination of the Size, Form, and Solvation of Macromolecules

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As has been shown in earlier work,¹ the molecular weight M of particles and the specific solvation volume s (the volume which corresponds to 1 gram of dissolved substance plus the solvent bound to it in the system) in a lyophilic colloid solution can be determined by means of osmotic measurements. This depends upon the fact that the osmotic pressure of such solutions is expressed by the equation:

$$P_0(1 - cs) = \frac{c}{M} RT \quad (1)$$

On the other hand, according to Eisenschitz,² the relative viscosity of a suspension of elongated particles is represented by the equation:

$$\eta_{rel} = 0.159cs \frac{l}{d \log \frac{2l}{d}} + 1 \quad (2)$$

where l is the length, and d is the short axis of the particles. If it could be proved that the specific solvation volume s has the same value by the two methods of measurement, then the absolute dimensions of the particles in a colloidal solution could be obtained from parallel osmotic and viscosimetric measurements. This can now be done.

On the assumption that newly dissolved rubber molecules are fiber molecules³ and the s values from osmotic and viscosimetric measurements are the same, all factors on the right side of equation (2) can be obtained from osmotic and roentgenographic data. Consequently the η_{rel} value can be calculated in advance. The values thus calculated agree extremely well with the experimental values of the relative viscosity.

By way of example, osmotic measurements of a 0.25 per cent solution of rubber in benzene showed 7550 A. U. for the length of the particles and 6.15 A. U. for their diameter (including the solvation shell). It follows from this that the relative viscosity has according to equation (2) a value of 3.16, while the experimental value was 3.15. The corresponding values for a solution of rubber in benzene were $l = 6560$ A. U., $d = 53.3$ A. U., $\eta_{rel} = 2.63$ and experimentally 2.70.

Since it is thus proved that the solvation volumes by osmotic and viscosimetric methods are in agreement, the molecular size, form and solvation of substances can be determined by osmotic and viscosimetric measurements alone, where roentgenographic data are lacking. When applied to aged rubber solutions, this method indicated that the aging phenomena are very complex, because three wholly distinct reactions take place simultaneously: (1) a cracking of the large molecules; (2) chemical changes which are manifest in changes in the solvation values, and (3) parallel alignment of the fiber molecules to sheaf molecules containing up to ten individual molecules. It is possible by the methods described to distinguish quantitatively in every case these three phenomena, even when more than one of these

reactions takes place at the same time. This will be described in more detail in a forthcoming paper.

References

- ¹ G. V. Schulz, *Z. physik. Chem.*, **188A**, 237; **190** (1932).
- ² Eisenschitz, *Ibid.*, **188A**, 78 (1932). The equation is here expressed in somewhat different form from that originally published.
- ³ On the subject of fiber molecules see Staudinger, *Ibid.*, **188A**, 35 (1932).

Verification of the Specific Gravity of Rubber before and after Its Vulcanization

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Ditmar published in 1930 a paper¹ in which he tried to prove that raw rubber subjected to the process of vulcanization did not alter its specific gravity, but that a rubber compound—pure or with fillers—lowered its specific gravity, *i. e.*, increased in volume during vulcanization. Figures were given showing a volume increase of rubber with chalk, talc, or carbon black in 22 cases. As could be seen from a table given by him, carbon black behaved so that with the increase of the percentage of it, the percentage of the increase of volume diminished, whereas with chalk and talc the percentage of the increase of volume was proportional to the rise of the percentage of the filler.

Having frequent opportunity of observing the behavior of various rubber compounds, and finding that during vulcanization results are quite different, we have made a verification of the specific gravity of a great number of samples of various rubbers before and after vulcanization.

Vulcanization was carried out in all cases under identical conditions, *viz.*, in a hand press at a temperature of 145° C. for 20 minutes in a mold having 18 sockets in the shape of rings with sharp edges.

Such a ring, with an inside opening 10-mm. wide, has walls 5-mm. thick and a 35-mm. diameter (see drawing).

As will be seen from Table I, with the increase in the quantity of rubber the divergency of the specific gravity of the vulcanized material increases, *i. e.*, the volume of the vulcanizate decreases (see samples 7 and 6.) It is evident from it, too, that mineral fillers and carbon black do not influence the alteration of the specific gravity, and the growth of the latter takes place at the expense of the condensation of rubber during vulcanization, and further that the larger mass in a rubber compound is condensed, *i. e.*, the more rubber is present the greater the difference in the condensation of the whole body (rubber).

The data obtained disagree altogether with those of Ditmar in another respect also, for it can be seen from samples 1 and 3, as well as from 1 and 4 and 7 and 4 that rubber not carbon black is the determinant factor in the decrease of volume, and by comparing rubbers 2 and 6, as well as 4 and 5, it can be concluded that the condensation of rubber rises with the increase of zinc oxide.

It is of interest to note that fluctuations of the specific gravity among single samples of raw rubber coincide and correspond to the variations in the specific gravity of the vulcanizates of this rubber, *i. e.*, raw samples with low indices have also lower indices after their vulcanization.

It is worth mentioning that out of 1846 samples none showed an increase of vol-

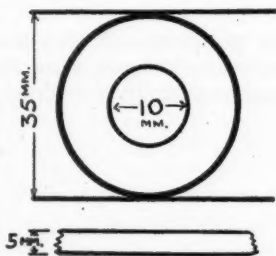


TABLE I

Sample Number	Rubber	Number of Samples	Specific Gravity of Raw Rubber	Average	Specific Gravity of Vulcanized Material	Average	Difference between Averages	Difference in Per Cent	Composition of Rubber in Per Cent
1	6.R.6. flipper	50	1.300-1.315	1.307	1.310-1.330	1.320	0.013	+0.91	R. 29, C. 17, ZnO 5.0, kaolin 12.0, reclaim
2	2.R.2 spreader for cord	110	0.990-1.005	0.997	1.015-1.040	1.027	0.030	+3.20	R. 80.6, ZnO 9.8, M.R.2, pine tar 2.4, vaseline 0.8
3	122 air tube	650	0.980-0.990	0.985	1.005-1.025	1.015	0.030	+0.324	R. 80, S. 8, ZnO 4.0
4	253 protector	700	0.995-1.115	1.105	1.110-1.155	1.122	0.017	+1.6	R. 63.5, C. 26.5, ZnO 4.0
5	Solid—for trucks and racers	110	1.205-1.285	1.240	1.265-1.305	1.285	0.045	+3.6	R. 53, C. 28, ZnO 14.4, MgO 1.0, coal tar 0.5
6	3.R.4. pads on cord	220	1.0 -1.025	1.012	1.055-1.080	1.067	0.055	+5.4	R. 80, ZnO 14.0, M.R. 1.3
7	202 gash sole	6		1.410		1.460	0.050	+1.03	R. 27, CaO 30.0, C. 5.5, reclaim 27.0

Note.—In this table R. means rubber; C., carbon black.

ume after vulcanization in a mold under pressure. The results of vulcanization without a press were formerly demonstrated by Bysow in his comprehensive work on the nature of vulcanization.²

As he maintains there a change in the volume of goods occurs after vulcanization. As shown by the experiments on two samples, given below, the specific gravity of the rubber-sulfur compound increases with the rise of the degree of vulcanization, which points to the condensation of the system.

TABLE II GIVEN BY BYSOW

Period of Time of Vulcanization, Min.	Compound A	Compound B
15	1.129	1.1975
30	1.154	1.2030
45	1.170	1.2035
60	1.170	1.2045
120	1.194	1.2180
180	1.192	1.2230

In these cases also the experiments have shown not an increase of volume, but on the contrary, a decrease. The specific gravity of all 1846 samples, before and after vulcanization, has been determined under identical condition in ZnCl_2 solutions by the same workers.

Conclusions

1. Every hot vulcanization of a rubber compound leads to a volume decrease of the vulcanized material, or to an increase of its specific gravity.
2. The increase of the specific gravity of a rubber system depends directly on the condensation of rubber only, and does not depend on fillers.
3. The extent of the increase of the specific gravity of a vulcanized material is proportional to the quantity of rubber in the compound and to the degree of vulcanization.
4. Active fillers, as ZnO , and accelerators can influence the growth of the specific gravity of a vulcanized compound as agents promoting vulcanization; hence carbon black, contrary to Ditmar's opinion, can hardly contribute to condensation.

References

- ¹ Ditmar, *Rubber Age* (N. Y.), **27**, 595 (1930).
- ² *Journal of the Chemico-Physical Society*, **1923**.

The Reinforcing Action and Other Properties of Titanium Fillers in Rubber Stocks

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Introduction

Titanium pigments have achieved success in the paint industry by virtue of their high covering power, good color, and resistance to hydrogen sulfide. The requirements of pigments for rubber are similar, and titanium whites have been employed to a limited extent in the rubber industry. The development of titanium fillers for rubber has, however, been slow, and a search of the literature only reveals a few references dealing with pigmentary properties.

Several papers by Ditmar and his collaborators in 1928-29 (summarized in *Kautschuk*, 5, 79, 1929), emphasize the non-toxic nature of titanium dioxide, its plasticizing action during mastication and the whiteness of titanium stocks cured with tetramethylthiouramdisulfide or hexamethylenetetramine. Reference is made to the reinforcing action of titanium fillers in a paper by Dawson (*India Rubber J.*, 79, 815), who studied the physical properties of vulcanized stocks made with titanium dioxide and two grades of titanium white. With an unaccelerated base mix requiring approximately 3 hours at 60 lbs. steam pressure, the titanium fillers, unlike zinc oxide and magnesium carbonate, did not activate vulcanization, and gave rubber of lower tensile strength than anticipated.

It was thought that with suitably accelerated mixes, titanium pigments might exhibit more pronounced reinforcement, when the growing demand for high grade white rubber products would render titanium white of special interest to the rubber industry.

Experimental

Master batches of pale crepe, accelerators, and sulfur were prepared for each set of mixes, on 12-in. rolls, initially at 50-55° C., with a friction speed ratio of 2 to 1. The batches were then divided and to equal portions were added 5, 10, and 20 volumes, respectively, of zinc oxide ("White Seal"), titanium dioxide, and titanium white. After resting for about 24 hours, these mixes were vulcanized in ring molds in a daylight press. Tensile tests were made on standard ring samples on the Schopper machine, extension being at the rate of 700 per cent elongation per minute, and the highest figure recorded with four rings was taken in each case.

Aging tests on samples vulcanized approximately to their optimum cure were carried out in the Geer oven at 82.5° C. for 5 days; this being adopted as a severe test for any vulcanized rubber not containing antioxidants. The inner discs cut by the Schopper punch were used as test pieces for water absorption determinations. Samples of known gage and surface area were weighed before and after various periods of immersion in distilled water at room temperature and at 60° C., and their increase in weight calculated as mg. per sq. decm. of surface.

Throughout the experiments, the pigmentary values of the fillers were compared by visual examination of the freshly cut edges of Schopper disc samples.

The mixes employed are given in Tables I and II, the first series being entirely

mercaptobenzothiazole mixes. Preliminary work with compounds C1, C2, and C3 showed that, in contrast with zinc oxide, neither titanium dioxide nor titanium white activated captax. Therefore 3 per cent of zinc oxide was added to mixes C₄ and C₅, in order to activate the accelerator, but these stocks were soft and weak after vulcanization. In a further series of mixes C₆ to C₁₁, 5 per cent of zinc oxide was added; and as the value of stearic acid in conjunction with mercaptobenzothiazole is recognized, a comparison of mixes with and without 2 per cent of stearic acid was made.

TABLE I

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
Pale crepe	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	60	3	3	125	5	5	125	5	5
Titanium dioxide	..	40	..	80	80	80	..
Titanium white	42	..	84	84	84
Sulfur	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Stearic acid	2	2	2
Mercaptobenzothiazole	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE II

	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13	D14
Pale crepe	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	3	63	123	3	3	3	3	3	33	63	3	3	3	3
Titanium dioxide	40	80	20	40
Titanium white	42	84	28	42
Sulfur	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Magnesia	1	1	1	1	1	1	1
Diphenylguanidine	1	1	1	1	1	1	1	1	1	1	1	1	1	1

The mixes given in Table II, contained diphenylguanidine as accelerator. A master batch containing no magnesia was used for mixes D1 to D7, and another containing 1 per cent of calcined magnesia was employed for compounds D8 to D14.

Aging tests were carried out on the vulcanizates containing diphenylguanidine. Four samples of each mix were given the approximate optimum cure of 45 minutes at 40 lbs. steam pressure, and then placed in the Geer oven at 82.5° C. for 5 days. After resting for two days, tensile tests were made as on the unaged samples and the deterioration calculated in terms of tensile product. The series of mixes (D2 to D7) containing no magnesia was used for water absorption tests. Two sets of samples of mixes (D2 to D7), were immersed in water, one set at room temperature and the other set at 60° C., and weighed periodically up to 14 days.

Results

The results of tensile tests described above are set out in Tables III, IV, and V, the following abbreviations being used: Modulus in kg. per sq. mm. to produce an elongation of 400 per cent, M400; tensile strength in kg. per sq. mm., T.S.; length at break as percentage of original length, L.B.; tensile product = tensile strength × length at break, T.P.

The resistance to aging of vulcanized mixes containing titanium dioxide, titanium white, and zinc oxide, is expressed as percentage deterioration of physical properties brought about by five days' Geer aging at 82.5° C. and the results are set out in Table VI.

Water absorption values of the vulcanized mixes (D2-D7) are calculated as gain in weight of the samples in mg. per sq. decm. of surface, when immersed in water at 18° C. and 60° C., respectively (see Table VII.)

TABLE III

Time of Cure at 135° C., Min.		TABLE III								
		Titanium Dioxide			Titanium White			Zinc Oxide		
		C4	C1	C10	C5	C8	C11	C6	C9	
30	M 400	0.44	0.45	0.52	0.65	0.63	
	T. S.	1.26	1.57	1.47	1.75	1.95	
	L. B.	745	770	735	730	755	
	T. P.	940	1210	1080	1280	1470	
45	M 400	0.65	0.59	0.50	0.72	0.48	0.57	0.57	0.65	
	T. S.	0.98	1.03	1.28	1.51	1.33	1.25	1.56	1.42	
	L. B.	710	730	715	785	750	650	720	680	
	T. P.	695	750	925	1180	1000	810	1050	970	
60	M 400	0.57	0.61	0.65	0.72	
	T. S.	0.91	0.97	1.30	1.21	
	L. B.	730	750	770	770	
	T. P.	660	730	1000	930	

(a) *Reinforcing Properties of Titanium Fillers in Rubber.*—In mixes vulcanized with mercaptobenzothiazole as accelerator, titanium dioxide does not give as good reinforcement as does zinc oxide. Titanium white, containing 74 per cent of barium sulfate, gives better tensile properties than those obtained with titanium dioxide at high loadings but is still inferior to zinc oxide as a reinforcing agent. The addition of stearic acid gives some improvement in tensile properties of both titanium dioxide and zinc oxide stocks, probably owing to better dispersion of the fillers; but there is no improvement with titanium white.

When tensile products are plotted against volume loading, it is seen that titanium white gives better reinforcement than zinc oxide in stocks vulcanized with diphenylguanidine, although pure titanium dioxide is inferior to zinc oxide at high loadings.

This superiority of titanium white over titanium dioxide is surprising in view of the poor reinforcing properties of barytes and lithopone. Recent x-ray investigations, however, carried out at the National Physical Laboratory (*Chem. Age*, **24**, 397 (1931)) on titanium whites and lithopone, provide a possible explanation of these results, for it is shown that titanium white is a particularly intimate mixture of titanium dioxide and barium sulfate, of which heat treatment decreases the grain size.

The addition of 1 per cent of magnesia to mixes containing diphenylguanidine improves those reinforced with zinc oxide but not the corresponding titanium compounds. This suggests that zinc oxide is more sensitive than titanium dioxide to acidity present in the mix or developed by the action of moisture on basic sulfates during vulcanization. Taute (*Farb. Lack*, **35**, 491 (1930)) reached a similar conclusion from surface energy measurements of the wetting of zinc oxide and titanium dioxide by organic liquids. He considered that the surface energies of the two oxides were similar and differences which arose when incorporated in rubber were entirely due to the greater basicity of zinc oxide.

(b) *Effect on Accelerators.*—Titanium fillers are more satisfactory in accelerated mixes than in unaccelerated compounds. They do not appreciably affect the rate of vulcanization even when heavy loadings are employed, but unlike zinc oxide they are not activators of vulcanization, and from 3 to 5 per cent of zinc oxide is desirable in all accelerated titanium stocks.

With mercaptobenzothiazole as accelerator, high loadings of titanium dioxide give soft vulcanizates with relatively low tensile strengths. This tendency may be connected with the recognized plasticising action of titanium dioxide during mixing (Ditmar, *loc. cit.*), and with the softness of products frequently associated with accelerators of this type.

TABLE IV

Time of Cure at 141.5° C., Min.		Blank D1	Titanium Dioxide		Titanium White		Zinc Oxide	
			D4	D5	D6	D7	D2	D3
30	M 400	0.175	0.48	0.84	0.33	0.57	0.42	0.96
	T. S.	1.68	2.0	1.67	1.97	1.90	1.77	2.0
	L. B.	900	795	635	830	750	755	670
	T. P.	1510	1550	1060	1630	1430	1340	1340
45	M 400.	0.25	0.57	0.94	0.43	0.74	0.54	1.05
	T. S.	2.0	2.0	1.5	2.1	1.84	1.90	1.92
	L. B.	838	735	610	800	700	730	635
	T. P.	1675	1470	915	1680	1290	1390	1220
60	M 400	0.68	0.48	0.70
	T. S.	1.56	1.64	1.66
	L. B.	660	725	667
	T. P.	1030	1190	1110

TABLE V

Time of Cure at 141.5° C., Min.		Blank D8	Titanium Dioxide		Titanium White		Zinc Oxide	
			D11	D12	D13	D14	D9	D10
30	M 400	0.27	0.30	0.29	0.31	0.29	0.48	0.60
	T. S.	1.63	1.80	1.47	1.95	1.57	1.96	2.10
	L. B.	885	850	835	860	855	765	730
	T. P.	1440	1530	1230	1680	1340	1500	1560
45	M 400	0.21	0.27	2.28	0.27	0.27	0.57	0.54
	T. S.	1.70	1.82	1.34	1.8	1.54	1.97	1.84
	L. B.	900	875	820	880	850	730	675
	T. P.	1530	1600	1100	1580	1320	1440	1240

TABLE VI

		Base Mix				
		Volume Loading	Before		After	% of Original
Nil	M 400		0.22	
Blank	T. S.		1.71		0.20	12
Containing magnesia	L. B.		900		460	51
	T. P.		1540		95	6

		Titanium Dioxide			Titanium White			Zinc Oxide		
5 volumes containing magnesia	M 400	0.26	0.35	..	0.26	0.33	..	0.57	0.63	..
	T. S.	1.82	0.35	19	1.80	0.33	18	1.97	1.18	60
	L. B.	880	525	60	880	525	60	730	610	84
	T. P.	1600	185	12	1580	175	11	1440	725	50
10 volumes, no magnesia	M 400	0.57	0.61	..	0.44	0.44	..	0.55	0.61	..
	T. S.	200	0.77	38	2.20	0.93	42	1.90	0.93	49
	L. B.	735	575	78	800	680	85	730	590	81
	T. P.	1470	40	30	1680	560	33	1390	550	40
20 volumes, no magnesia	M 400	0.93	0.92	..	0.74	0.68	..	1.10	1.13	..
	T. S.	1.50	0.98	65	1.84	0.97	53	1.92	1.16	41
	L. B.	610	530	87	700	608	87	635	520	82
	T. P.	915	520	57	1290	890	46	1220	600	48

TABLE VII

	Titanium Oxide		Titanium White		Zinc Oxide	
	10 Vols.	20 Vols.	10 Vols.	20 Vols.	10 Vols.	20 Vols.
7 days' immersion	55	43	53	60	70	65
14 days' immersion	75	58	88	85	110	105
7 days' immersion at 60° C.	220	195	300	310	375	365
14 days' immersion at 60° C.	330	300	470	480	575	560

(c) *Aging Properties.*—Titanium fillers in heavily loaded compounds give about the same resistance to aging as zinc oxide.

At 5 and 10 volume loadings, however, zinc oxide confers better aging properties, particularly when 1 per cent of calcined magnesia is present. Titanium dioxide is slightly superior to titanium white in giving better aging resistance over the whole range of loadings.

(d) *Water-Resistance.*—Water-immersion tests comparing compounds loaded with titanium and zinc fillers show that the former confer better water-resisting properties. Secondly, as stated above with respect to aging resistance, compounds containing titanium dioxide are more resistant to water than those containing titanium white. Thirdly, the influence of volume loading is of minor importance, 20 volume mixes differing only slightly from 10 volume mixes in this respect.

These conclusions are in accordance with those reached by Winkelmann and Croakman (*Rubber Age* (New York) 29, 430 (1931)), who found that zinc oxide, clay, and to a lesser extent barytes, caused marked increase in water absorption, while inactive fillers such as carbon black give good water-resisting properties. It seems probable that the inert non-basic character of titanium dioxide gives rise to less affinity for water than that of zinc oxide, and consequently to superior water-resistance of compounds loaded with titanium dioxide.

(e) *Pigmentary Value.*—Examination of the whiteness of freshly cut edges of the vulcanizates throughout the experimental work showed that: (1) mixes vulcanized with mercaptobenzothiazole were generally whiter than those containing diphenylguanidine; (2) the incorporation of stearic acid to improve the physical properties of the mixes produced a yellowish discoloration of the vulcanizates; (3) mixes containing 10 volumes of titanium pigments were whiter than those containing 20 volumes of zinc oxide; (4) titanium dioxide was slightly more effective as a pigment than titanium white. The poor pigmentary qualities of barium sulfate in rubber would suggest that 74 per cent of this ingredient present in titanium white would make the latter a relatively poor pigment. The smallness of the difference between the pigmentary properties of titanium dioxide and titanium white is regarded as further evidence of the intimate combination of barium sulfate and titanium dioxide in the white.

Summary of Conclusions

(1) The reinforcing properties of a high-grade titanium white, containing 74 per cent barium sulfate in intimate combination with the oxide, are slightly better than those of "White Seal" zinc oxide in mixes vulcanized with diphenylguanidine.

(2) Titanium dioxide is generally inferior to titanium white as a reinforcing agent, and at high loadings gave poor tensile properties, especially in compounds accelerated with mercaptobenzothiazole.

(3) The titanium fillers are incapable of behaving as activators of organic accelerators, as zinc oxide does, and from 3 to 5 per cent of zinc oxide is required in the majority of titanium stocks containing organic accelerators.

(4) The aging properties of compounds reinforced with titanium fillers are generally similar to those conferred by zinc oxide, but are inferior to the latter at low volume loadings.

(5) Better pigmentary and water-resisting properties are conferred by titanium dioxide than by titanium white, and both these fillers are superior to zinc oxide in these respects.

Influence of Oxygen on the Degradation of Rubber Solutions

Paul Bary and Émile Fleurent

The publications of Staudinger, of Dufraisse and Drisch, and of other authors have called attention to the pronounced effect of oxygen on the rigidity of rubber and on the viscosity of its solutions.

In our preceding papers,¹ we have shown that the degradation of rubber solutions in different solvents at different temperatures and concentrations, in all cases in the presence of oxygen—even in very small proportions, approaches a limiting viscosity of the same order of magnitude as that of the solvent used.

We have now carried out a new series of experiments on several solutions of different concentrations of plantation rubber (in the form of smoked crepe) in xylene. The work was done in tubes sealed after prolonged evacuation. Ten sealed tubes were prepared for each concentration and for each temperature, and were placed together in the oven at a temperature of 44° and also at 92° C. After varied periods of heating, one tube from each series was taken, was allowed to cool to 20° C., and the rate of flow through a capillary tube was then determined. The ratio of the time of flow of the solution to that of the pure solvent was considered to be the relative viscosity.

Under these conditions it was observed that the degradation of rubber in solution no longer approached, as had been previously observed in the presence of oxygen, a limit corresponding to a relative viscosity of unity, but approached a limiting degradation, the magnitude of which was the smaller the greater the concentration of the rubber solution and the lower the constant temperature of heating.

This long series of experiments has again shown the marked influence of traces of oxygen which, in certain cases and in spite of great precautions, made it necessary to discard tubes of which the viscosity values were much lower than those obtained with longer periods of heating. These results led us to eliminate a certain number of determinations and, since there were in each series only ten measurements in all for the different periods of heating, the series of twelve which were undertaken, but not yet completed, left fewer well-defined results than had been anticipated.

Certain conclusions can, however, be drawn from the work. The curve of the degradation as a function of the time can be expressed in every instance by a hyperbolic law such as:

$$\eta - \eta_{\infty} = \frac{A}{t + \theta}$$

where η is the relative viscosity after the time t , η_{∞} is the limiting viscosity, and A and θ are constants. The following table gives the values of η_{∞} , A , and θ , making it possible to find by calculation the observed values of η with deviations of the same order of magnitude as the experimental errors.

Temp. in ° C.	Percentage Concentration	A	θ	η_{∞}
44	{ 3.0	124,000	1150	100.0
	{ 2.0	29,400	282	34.9
	{ 1.5	64,170	2750	7.9
92	{ 3.0	7,380	33.1	10.9
	{ 2.0	2,595	167.0	4.8

The values of η_{∞} thus found when heating was carried out at 44° for 5700 hours and at 92° for 4000 hours show that the limit which the degradation approaches corresponds to a viscosity which diminishes with decrease in the concentration of the solution and with increase in the temperature.

This limit, at which η_{∞} reaches 1 when oxygen is present, is attained much more rapidly under this latter condition.

Reference

¹ *Compt. rend.*, **192**, 946 (1931); **193**, 852 (1931); *RUBBER CHEMISTRY AND TECHNOLOGY*, **4**, 505 (1931); **5**, 121 (1932).

Roentgenographic Examination of μ -Polychloroprene ($\text{CH}_2:\text{CClCH}:\text{CH}_2$)_x

P. Garbsch and G. v. Susich

THE I. G. FARBENINDUSTRIE A.-G. LUDWIGSHAFEN, A. RHEIN

μ -Polychloroprene (polymeric 2-chloro-1,3-butadiene or "Duprene"), recently described by Carothers, Williams, Collins and Kirby,¹ shows in the unstretched state an amorphous x-ray picture and when stretched a well-defined fiber diagram. Since a crystallization and parallel orientation of this kind upon stretching had not been observed previously in any natural or artificial product² other than natural rubbers (smoked sheet, latex film, amorphous crepes), although some of these products may be highly elastic and may even split apart into fibers in the cold, the x-ray diagram makes possible a rapid and certain identification of the μ -polychloroprene.

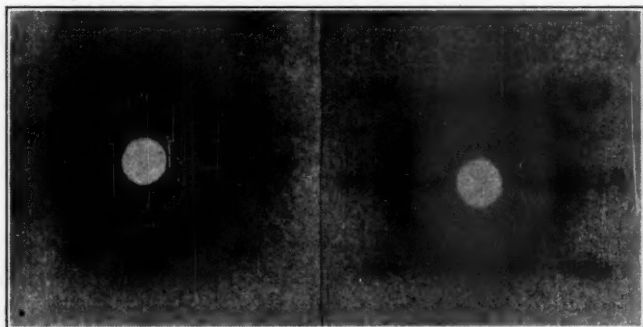


Figure 1—Unstretched μ -Polychloroprene
Amorphous Diagram

Figure 2—Stretched μ -Polychloroprene
Fiber Diagram

The experimental material was a μ -polychloroprene with 40.3 per cent chlorine (the theoretical chlorine content of $(\text{C}_4\text{H}_5\text{Cl})_x$ is 40.1 per cent) which had been prepared from vinylacetylene by addition of hydrochloric acid according to the equation: $\text{CH}:\text{CCHCH}_2 + \text{HCl} \rightarrow \text{CH}_2:\text{CClCH}:\text{CH}_2$. This substance was very elastic and "nervy." It was light brown and probably still contained small quantities of monomeric and low polymeric chloroprene.

Figure 1 shows the amorphous x-ray diagram of unstretched μ -polychloroprene, from which an average molecular weight of 4.8 ± 0.1 A. U. can be calculated. The fiber diagram of the stretched pieces (about 600 per cent elongation) is shown in Fig. 2. The fiber period was calculated at 4.81 ± 0.03 A. U. from Table I. These data agree well with the results of the American investigators. Naturally the fiber diagram of μ -polychloroprene is wholly unlike that of natural rubber. It should be mentioned that the fiber period of natural rubber is 8.38 ± 0.15 , of α -gutta-percha 8.78 ± 0.12 and of β -gutta-percha 4.87 ± 0.07 A. U.

The behavior of μ -polychloroprene during elongation is therefore exactly like that of amorphous natural rubbers, i. e., crystallization takes place simultaneously with the fairly complete fiber orientation at a definite degree of elongation (at about 200 per cent elongation, according to the experimental conditions and the quality of the material). The crystalline interferences disappear with increase in temperature and with swelling. Until now it has not been possible to crystallize μ -polychloroprene by cooling to low temperatures, so that in this respect, too, its behavior is similar to that of amorphous natural rubbers. It still remains to be seen whether, as in the case of frozen rubber and of crystallized crepe, long standing or the removal of components which hinder crystallization, will make possible crystallization without stretching. Higher degrees of orientation which allow a trustworthy determination of the dimensions of the elementary substance have not yet been obtained.

TABLE I
CALCULATION OF THE FIBER DIAGRAM
Distance 32.8 ± 0.3 mm. Cu-K Radiation

	Intensity	2c	2a	2b	Lattice Plane Distance d in A. U.	Identity Period I in A. U.
		in Mm.				
Equator	Strong	21.6			4.42 β	
	Very strong	24.1			4.39 α	
	Medium	26.8			3.97 α	
	Medium	32.8			3.33 α	
	Very weak	38.0			2.97 α	
I.						
Hyperbola ("Schichtlinie")	Strong	24.6	10.0	22.8	4.32 α	4.78 } 4.81
	Feebly diffused	38.0	29.0	24.0	2.97 α	4.82 } +
	Feebly diffused	42.0	34.0	24.5	2.75 α	0.03 }

References

- ¹ Carothers, Williams, Collins and Kirby, *J. Am. Chem. Soc.*, **53**, 4203 (1931).
- ² Katz, *Kautschuk*, **3**, 215 (1917); Mark, *Ergebn. tech. Roentgenkunde*, **1**, 142 (1930).

[CONTRIBUTION No. 98 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

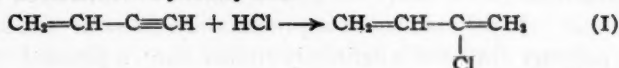
HOMOLOGS OF CHLOROPRENE AND THEIR POLYMERS (SECOND PAPER ON NEW SYNTHETIC RUBBERS)

BY WALLACE H. CAROTHERS AND DONALD D. COFFMAN

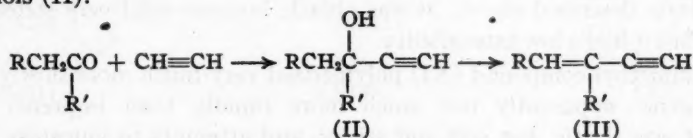
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Chloroprene (chloro-2-butadiene-1,3, I) is obtained by the addition of hydrogen chloride to vinylacetylene.¹



In the rate of its spontaneous transformation into a rubber-like polymer it greatly exceeds all previously described dienes.² The present paper is concerned with homologs of chloroprene obtained by the addition of hydrogen chloride to homologs of vinylacetylene. As Merling has shown,³ compounds (III) of the latter class can be obtained by the action of sodium acetylide on aldehydes or ketones, followed by dehydration of the resulting carbinols (II).



These reactions were in fact proposed as steps in a process for the synthesis of rubber, since in the case where $\text{R} = \text{H}$ and $\text{R}' = \text{CH}_3$, the product II can be reduced to the vinylcarbinol and then dehydrated to produce isoprene. The elegance of this method has been frequently commended, but from our own experience it appears more elegant than useful, since the yields in the first step were rather low. Nevertheless, the isolation of small amounts of the pure carbinols presents no particular difficulties, and under properly selected conditions the dehydration to the substituted vinylacetylene proceeds fairly smoothly.

In the present study the carbinols used were those represented in formulas IV-VI. These and the corresponding vinylacetylenes (VII-IX) have already been described by Merling.³ The substituted vinylacetylenes were converted into the corresponding substituted chloroprenes (X-XII) by shaking them at room temperature with concentrated hydro-

¹ Carothers, Berchet and Collins, *THIS JOURNAL*, 54, 4066 (1932).

² Carothers, Williams, Collins and Kirby, *ibid.*, 53, 4203 (1931).

³ Merling, Friedr. Farbenfab. von Bayer & Co., German Patents 280,226, 285,770, 286,920, 288,271; Scheibler and Fischer, *Ber.*, [2] 55, 2903 (1922); Sung Wouseng, *Ann. chim.*, [10] 1, 343-416 (1924).

chloric acid containing cuprous chloride and ammonium chloride. The reactions proceeded somewhat more slowly than the formation of chloroprene itself by the same process. The yields obtained were rather low but this was due chiefly to incomplete conversion. The substituted chloroprenes reacted smoothly with α -naphthoquinone to form crystalline addition products (XIII-XV), which were readily oxidized to the corresponding anthraquinones (XVI-XVIII).

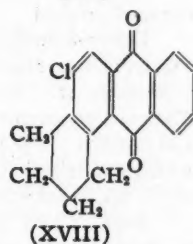
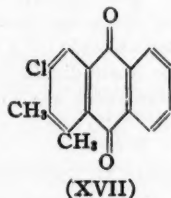
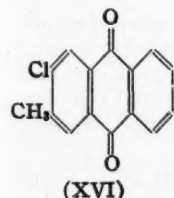
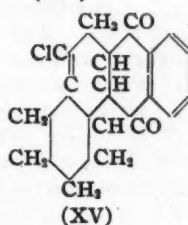
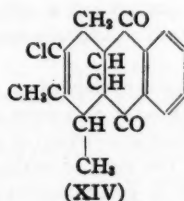
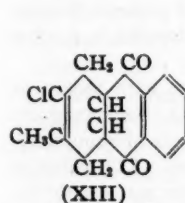
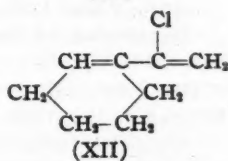
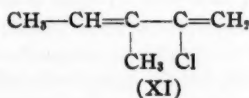
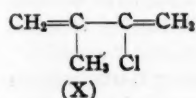
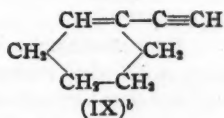
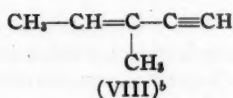
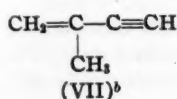
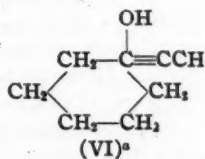
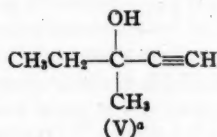
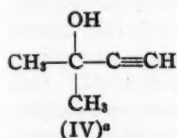
The amounts of the substituted chloroprenes available did not suffice for a very detailed study of their polymerization. The results obtained, however, indicated quite definitely that, of the three dienes, only chloro-2-methyl-3-butadiene (X) is likely to deserve serious consideration as a precursor of rubber. It polymerizes at approximately the same rate as chloroprene; the polymer obtained is definitely rubber-like; a plastic form of the rubber-like product is readily isolated by distilling the unchanged diene from the viscous sirup or the soft jelly obtained by incomplete polymerization; this plastic material is vulcanized by the action of heat alone without the addition of sulfur. Samples thus obtained were strong, very tough and quite elastic, but their extensibility was rather low. The ultimate product of the spontaneous polymerization of the diene in a sealed tube containing a very little air was rather similar in its properties to the vulcanizate described above; it was a black, lustrous solid very strong and tough, but it had a low extensibility.

The dimethyl compound (XI) polymerized very much more slowly than chloroprene—apparently not much more rapidly than isoprene. The product was elastic, but soft and sticky, and attempts to vulcanize it resulted in only partial loss of the plastic properties. The vulcanizate was coherent and rather strong; its extensibility was fairly high (about 500%) but recovery from stretch was slow.

The tetramethylene compound (XII) also polymerized very slowly, and the product obtained was a very soft and plastic mass. The attempt to vulcanize it was almost entirely unsuccessful; the plastic properties were not appreciably affected, but after standing for several months the compounded sample had become quite brittle although it contained an antioxidant.

These observations together with others already available permit some conclusions concerning the effect of the position and the nature of substituting groups on the polymerization of butadiene. Since butadiene, isoprene, and β,γ -dimethylbutadiene do not very greatly differ in the rate of their spontaneous polymerization, it is evident that methyl is not an activating group. The fact that chloroprene polymerizes about seven hundred times as fast as isoprene illustrates the powerful activating effect of a chlorine atom at the β -position. The introduction of a methyl group at the other interior carbon does not greatly modify this effect, although the polymer obtained is somewhat less extensible; but the introduction of a

second methyl group at one of the terminal carbons almost completely checks the activating effect of the chlorine atom.



^a See Friedr. Farbenfab. von Bayer & Co., German Patents 280,226, 284,764, 286,920, 289,800. ^b German Patent 290,558.

Experimental Part

Acetylenic Carbinols.—The general method used for the preparation of the acetylenic carbinols has already been described in the literature.⁴ The ketone (2 moles) was slowly introduced into an ethereal suspension (1 l. abs. ether) of sodamide (2 moles) at -10° with vigorous agitation. After five hours, when the evolution of ammonia had become very slow, acetylene was passed during eight hours into the reaction mixture at -10° , under 10–15 pounds pressure with constant shaking. The reaction mixture was then poured onto crushed ice, acidified with dilute sulfuric acid, subjected to ether extraction, the extract dried and distilled. The yields were: ethynyl-di-

⁴ Sung Wouseng, *Ann. chim.*, [10] I, 343–416 (1924).

methylcarbinol (IV), b. p. 104–108°, 36%; ethynylmethylethylcarbinol (V), b. p. 119–123°, 33%; ethynyl-1-cyclohexanol-1 (VI), b. p. 174° at 760 mm., 53–55° at 2 mm., 50%.

In the preparation of ethynyl-1-cyclohexanol-1 two by-products were isolated and identified: di-(hydroxy-1-cyclohexyl-1)-acetylene (10 g. from 2 moles of the ketone); crystals from carbon tetrachloride or benzene-petroleum ether, m. p. 106–107° (copper block). The literature records its melting point as 102°.⁵

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.65; H, 9.90. Found: C, 74.74; H, 10.41.

Cyclohexylidene-2-cyclohexanone-1 (35 g. from 4 moles of the ketone), colorless liquid (b. p. 143–145° at 16 mm.; n_D^{20} 1.5049; d_4^{20} 1.001) which readily formed an oxime, m. p. 146°.⁶

Ethynylmethylphenylcarbinol.—The condensation of acetylene with acetophenone gave in 2% yield ethynylmethylphenylcarbinol which boiled at 69° under 1 mm. The carbinol after three crystallizations from petroleum ether (b. p. 40–60°) melted at 52–53°.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.19; H, 6.85. Found: C, 81.71; H, 6.88.

Dehydration of the Acetylenic Carbinols.—The ethynyldimethylcarbinol was heated at 90° (bath) in a distilling flask with an equal weight of *p*-toluenesulfonic acid for three hours. The methyl-2-butene-1-ine-3 (VII) distilled into the receiver as it was formed, b. p. 34°; yield, 53%.

The ethynylmethylethylcarbinol (60 g.) was slowly added during thirty minutes to 10 g. of *p*-toluenesulfonic acid contained in a distilling flask surrounded by a water-bath at 80°. The operation was carried out at slightly diminished pressure and the methyl-3-pentene-2-ine-4 (VIII) distilled into the receiver as it was formed, b. p. 68 to 71° at 760 mm.; yield, 25%.

Attempts to dehydrate ethynyl-1-cyclohexanol-1 by heating it with iodine, *p*-toluene-sulfonic acid, or anhydrous oxalic acid were unsuccessful, but excellent results were obtained by passing the carbinol in a stream of nitrogen over basic aluminum sulfate (from alum) at 240 to 260°. The yield of ethynyl-1-cyclohexene-1 (IX) boiling at 40 to 43° at 12 mm. was about 35% per passage and the remainder was chiefly unchanged carbinol.

Chloro-2-methyl-3-butadiene-1,3 (X).—Methyl-2-butene-1-ine-3 (40 g.) was shaken in a pressure bottle during four and a half hours at 20° with hydrochloric acid (105 cc., sp. gr. 1.19) containing cuprous chloride (15 g.) and ammonium chloride (6 g.). The reaction mixture was subjected to steam distillation, and the products were dried and distilled. The yield of the chlorobutadiene was 25 g. or 40%; b. p. 93° (760 mm.) with polymerization, 41° (113 mm.), 37° (105 mm.); n_D^{20} 1.4689, d_4^{20} 0.9593, M_R (obs.) 29.75, M_R (calcd.), 29.22.

Anal. Calcd. for C_4H_7Cl : C, 58.54; H, 6.83; Cl, 34.63; mol. wt. 103. Found: C, 58.55; H, 6.72; Cl, 34.39; mol. wt. (in freezing benzene), 126.

Chloro-2-methyl-3-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XIII).— α -Naphthoquinone (0.5 g.) was heated at 100° for half an hour with chloro-2-methyl-3-butadiene-1,3 (1 g.). The reaction mixture was cooled and the crystals were washed with absolute methanol. After crystallization from aqueous acetone, the white needles melted at 165–166° (uncorr.).

Anal. Calcd. for $C_{15}H_{13}O_2Cl$: C, 69.09; H, 4.99. Found: C, 68.72; H, 4.86.

Chloro-2-methyl-3-anthraquinone (XVI).—The tetrahydro compound (XIII) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the blue solution until only a yellow color remained. The suspension was diluted with water, the yellow crystals were filtered and recrystallized from glacial acetic acid. The material

⁵ Iotsitch, *J. soc. phys.-chim. r.*, **38**, 656 (1906), G. Dupont, *Ann. chim.*, [8] **30**, 498 (1913).

⁶ Wallach, *Ber.*, **29**, 2965 (1896); Mannich, *ibid.*, **40**, 157 (1907).

melted at 214–215° (uncorr.). The melting point of chloro-2-methyl-3-anthraquinone is recorded in the literature as 215° and 219° corrected.⁷

Chloro-2-dimethyl-3,4-butadiene-1,3 (XI).—Methyl-3-pentene-2-ine-4 (25 g.) was shaken in a pressure bottle during five and a half hours at 20° with hydrochloric acid (58 cc., sp. gr. 1.19), containing cuprous chloride (8.5 g.) and ammonium chloride (3.5 g.). The reaction mixture was subjected to steam distillation and the product dried and distilled. The yield of the chlorobutadiene was 9 g. or 22%. A considerable proportion of unreacted hydrocarbon was recovered; b. p. 57–60° (96 mm.), n_D^{20} 1.4671; d_4^{20} 0.9437, M_R (obs.) 34.26, M_R (calcd.) 33.84.

Anal. Calcd. for C_6H_8Cl : C, 61.80; H, 7.72; Cl, 30.44; mol. wt., 116.5. Found: C, 61.40; H, 7.55; Cl, 29.24; mol. wt., 116.

Chloro-2-dimethyl-3,4-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XIV).— α -Naphthoquinone (0.5 g.) was heated at 100° during one hour with chloro-2-dimethyl-3,4-butadiene-1,3 (1 g.). The reaction mixture was cooled, and the crystals were washed with absolute methanol. After crystallization from aqueous acetone, the white needles melted at 107° (copper block).

Anal. Calcd. for $C_{18}H_{10}O_2Cl$: C, 69.95; H, 5.47. Found: C, 69.41; H, 5.53.

Chloro-2-dimethyl-3,4-anthraquinone (XVII).—The tetrahydro compound (XIV) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the purple solution until only a pale yellow color remained. The ethanol was diluted with water, the yellow crystals filtered and recrystallized from glacial acetic acid. The anthraquinone melted at 171.5° (copper block).

Anal. Calcd. for $C_{18}H_{10}O_2Cl$: C, 70.98; H, 4.07. Found: C, 70.22; H, 4.14.

Chloro-2-tetramethylene-3,4-butadiene-1,3 (XII).—Ethinyl-1-cyclohexene-1 (33 g.) was shaken in a pressure bottle during four and a half hours at 20° with hydrochloric acid (70 cc., sp. gr., 1.19) containing cuprous chloride (10 g.) and ammonium chloride (4 g.). The reaction mixture was subjected to vacuum steam distillation, and the product dried and fractionated. The yield of the chlorobutadiene was 14 g. or 32% of the theoretical, and a considerable amount of unreacted hydrocarbon was recovered; b. p. 55–57° (1 mm.); n_D^{20} 1.5240; d_4^{20} 1.0422; M_R (obs.), 41.84; M_R (calcd.), 40.88.

Anal. Calcd. for C_8H_8Cl : C, 67.37; H, 7.72; mol. wt., 142.5. Found: C, 67.50; H, 7.90; mol. wt. (in freezing benzene), 143.

Chloro-2-tetramethylene-3,4-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XV).— α -Naphthoquinone (2 g.) was heated at 100° during twenty minutes with chloro-2-tetramethylene-3,4-butadiene-1,3 (4 g.). On cooling crystals formed which were washed with absolute methanol. After recrystallization from absolute ethanol, the white needles melted at 191–192° (copper block).

Anal. Calcd. for $C_{18}H_{12}ClO_2$: C, 71.88; H, 5.66. Found: C, 71.42; H, 5.86.

Chloro-2-tetramethylene-3,4-anthraquinone (XVIII).—The tetrahydro compound (XV) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the purple solution until only a yellow color remained. The ethanol was diluted with water, the crystals filtered and recrystallized from glacial acetic acid. The yellow needles melted at 155–156° (copper block).

Anal. Calcd. for $C_{18}H_{12}ClO_2$: C, 72.85; H, 4.38. Found: C, 72.59; H, 4.53.

Polymerization of Chloro-2-methyl-3-butadiene-1,3 (X).—When a sample of the diene was allowed to stand at the laboratory conditions in a sealed tube containing a trace of air it set up to a stiff jelly in about five days. Later the specimen became dark in color and ten months later when the tube was opened the product was a black, lustrous solid, very strong and tough but having only a slight extensibility. A sample of

⁷ Keimatsu and Hirans, *J. Pharm. Soc. Japan*, 49, 140–147 (1929).

the diene exposed to the light of a Cooper-Hewitt lamp (mercury arc in glass) at ordinary temperature contained 30% of polymer after sixty-five hours. (Under the same conditions chloroprene polymerizes at a greater rate than this—about 30% in forty hours.) The sample was then a soft jelly. The polymer was precipitated, washed with alcohol, and compounded with 1% of phenyl- β -naphthylamine, 5% of zinc oxide, 2% of stearic acid, and heated in a mold at 140 to 145° for fifteen minutes. The resulting sheet was coherent, strong, tough, and rather elastic, but it was deficient in resiliency and extensibility. It appears that the polymer from chloro-2-methyl-3-butadiene-1,3 more closely resembles the products from dimethylbutadiene (methyl rubber) than those obtained either from isoprene or from chloroprene.

Polymerization of Chloro-2-dimethyl-3,4-butadiene-1,3 (XI).—A specimen placed in a sealed glass tube under air and exposed to the light of a 100-watt Mazda lamp for two months at the ordinary temperature was converted to a very soft, sticky, elastic mass which still contained a considerable proportion of volatile material—apparently unchanged monomer. After standing for eight months more in the absence of direct light its properties had not undergone any further change.

A sample of the diene was submitted to a pressure of 8000 atmospheres for 106 hours at 40°. The product was a soft, plastic, elastic mass containing about 70% of polymer. It was compounded with 1% of phenyl- β -naphthylamine, 10% of zinc oxide, 2% of stearic acid, 1% of benzidine and 1% of tetramethylthiuramdisulfide and was then heated in a mold at 120 to 125° for seventy minutes. The product obtained in this way was rather soft and lacking in resiliency and nerve. The extensibility was fairly high (400 to 500%).

Polymerization of Chloro-2-tetramethylene-3,4-butadiene-1,3 (XII).—A specimen in a glass tube under air was exposed to the light of a 100-watt Mazda light for forty-eight days. The product was a thick, dark mass. Removal of the unchanged monomer by washing with alcohol yielded about 70% of polymer. This was very soft, plastic and sticky. It was compounded in the same manner as the polymer described in the preceding paragraph, but after being heated it still remained soft and plastic. After standing for ten months it had become brittle. A specimen of the diene was submitted to a pressure of 6000 atmospheres at 38° during ninety-six hours. The product was quite soft and plastic and when compounded as in the preceding example and heated for seventy minutes at 120° it showed no appreciable signs of vulcanization.

We are indebted to Dr. H. W. Starkweather for the experiments at high pressures.

Summary

Three substituted vinylacetylenes were treated with hydrogen chloride and thus converted to the corresponding chlorobutadienes. Chloro-2-methyl-3-butadiene-1,3 polymerized very rapidly and yielded a rubber-like polymer, which after vulcanization was less extensible than the corresponding product obtained from chloroprene (chloro-2-butadiene-1,3). Chloro-2-dimethyl-3,4-butadiene-1,3 polymerized very slowly and the product, even after vulcanization, was soft and lacking in nerve. Chloro-2-tetramethylene-3,4-butadiene-1,3 also polymerized very slowly and the product was very soft, plastic and sticky.

The structures of the three new chlorobutadienes were established through their reaction with α -naphthoquinone to form crystalline addition products, which were oxidized to the corresponding anthraquinones.

WILMINGTON, DELAWARE

[CONTRIBUTION No. 96 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

ACETYLENE POLYMERS AND THEIR DERIVATIVES. III. THE ADDITION OF HYDROGEN CHLORIDE TO VINYLACETYLENE

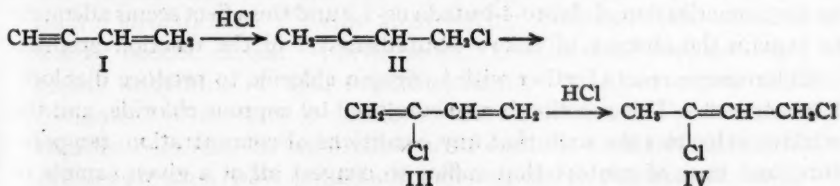
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Vinylacetylene (I) constitutes the simplest possible example of a conjugated enyne system. Recorded information concerning the addition reactions of such systems is exceedingly meager. It has already been reported¹ that chloroprene (chloro-2-butadiene-1,3, III) can be obtained by the addition of (aqueous) hydrogen chloride to vinylacetylene, and the present paper is concerned with a further description of the mechanism of this reaction and the nature of the products to which it leads.

It is shown that the initial step consists in 1,4 addition, and the primary product thus formed is chloro-4-butadiene-1,2 (II) (b. p. 88°), a new compound of rather unusual structure and curious properties. Under certain conditions this chloro-4-butadiene-1,2 can be isolated as the major reaction product, but it readily undergoes an isomerization involving migration of the chlorine atom and a shift of a double bond. Chloroprene (b. p. 59.4°) is formed thus, and the transformation occurs with such facility in the presence of hydrogen chloride that chloroprene always constitutes a part of the reaction product. Certain salts reinforce the catalytic effect of hydrogen chloride on this transformation, and when cuprous chloride is present no chloro-4-butadiene-1,2 is found in the reaction product. When sufficient amounts of hydrogen chloride are present the reaction proceeds further with the formation of dichloro-2,4-butene-2 (IV).



Influence of Conditions on the Reaction.—The reaction between vinylacetylene and hydrogen chloride is conveniently carried out in the following manner. Fifty grams of vinylacetylene and 175 cc. of concentrated hydrochloric acid (about 2.2 moles of hydrochloric acid) are placed in a pressure bottle, and the bottle is shaken to promote contact between the aqueous and the hydrocarbon layers. After the completion of the reaction the oily layer is separated, dried, mixed with a small amount of an anti-

¹ Carothers, Williams, Collins and Kirby, *THIS JOURNAL*, 53, 4203 (1931).

oxidant such as catechol or pyrogallol, and distilled *in vacuo* through an efficient column. Data from a very large number of experiments of this type are available. Owing to the fact that in most cases neither the temperature nor the speed of shaking was precisely controlled these data cannot be used as a basis for a quantitative description of reaction velocities; nevertheless, they give a clear idea of relative rates.

In a typical experiment of the kind described above, about 43% of the vinylacetylene was utilized in seven hours, and analysis of the reaction product yielded chloro-4-butadiene-1,2 and chloroprene in the ratio 2.2:1.

In general this ratio is diminished by increase in the temperature, concentration of hydrogen chloride, or time of contact; and the proportion of the chloro-4-butadiene-1,2 in the product is less the more completely the vinylacetylene is utilized. This fact demonstrates that part at least of the chloroprene is formed by the isomerization of the chloro-4-butadiene-1,2 during the course of the reaction, and it seems reasonable to conclude that all of it is formed by this demonstrated mechanism.

The reaction is considerably accelerated by the presence of certain salts. Thus when 25 g. of calcium chloride is present in the reaction mixture the time required to obtain 40% conversion is decreased by about one-half, but the ratio of the two isomeric chlorobutadienes present in the reaction product at a given percentage conversion remains practically unaffected. Cuprous chloride is a much more powerful catalyst. When 25 g. of this salt is present in the reaction mixture, about 90% of the vinylacetylene reacts in four hours at 20°. In this case the product consists for the most part of chloroprene, and no chloro-4-butadiene-1,2 is present. It is, however, not necessary to assume that the cuprous chloride directs the reaction so that addition occurs at the acetylenic linkage. Separate experiments show that cuprous chloride reinforces the catalytic effect of hydrogen chloride on the isomerization of chloro-4-butadiene-1,2 and this effect seems adequate to explain the absence of chloro-4-butadiene-1,2 in the reaction product.

Chloroprene reacts further with hydrogen chloride to produce dichloro-2,4-butene-2. This reaction is also catalyzed by cuprous chloride, and the relative velocities are such that any conditions of concentration, temperature, and time of contact that suffice to convert all of a given sample of vinylacetylene result in the formation of a certain amount of the dichlorobutene. The following experiment is illustrative. Fifty grams of vinylacetylene, 175 cc. of concentrated hydrochloric acid, 25 g. of cuprous chloride, and 10 g. of ammonium chloride were placed in each of forty bottles. The bottles were gently shaken in a bath at 20° for four hours and then allowed to stand for twelve hours at 0°. The contents of all the bottles were combined and the mixture was steam distilled *in vacuo* into a receiver placed at the bottom of a 2-meter jacketed, carborundum-packed column provided with a dephlegmator and a second receiver each cooled to -80°.

The pressure was kept at about 150 mm. until all of the unchanged vinylacetylene had collected in the second receiver, and the pressure was then gradually reduced to 10 mm. until all of the chloroprene had collected in the second receiver. The dichlorobutene remained in the first receiver. The yields were: unchanged vinylacetylene, 115 g.; chloroprene, 2862 g.; dichlorobutene, 117 g. In mole percentages these values are 5.7, 84.2, and 2.5, respectively. The deficit amounting to 7.6 mole per cent. was mostly comprised in intermediate fractions. When this deficit is distributed proportionately among the three major fractions, the percentage yields become: unreacted vinylacetylene, 6.1%; chloroprene, 91.2%; dichlorobutene, 2.7%. The corresponding figures for the calculated yields based upon unrecovered vinylacetylene are chloroprene, 97%, and dichlorobutene, 3%. Further experiments indicate that the conditions of this experiment lie very close to the optimum for the conversion of vinylacetylene to chloroprene in a batch process: a higher ratio of chloroprene to dichlorobutene can be obtained only by utilizing a smaller proportion of the applied vinylacetylene, and a more complete utilization of the vinylacetylene results in a larger proportion of dichlorobutene.

The Properties of Chloro-4-butadiene-1,2 and the Proof of its Structure.—Chloro-4-butadiene-1,2 is a colorless liquid boiling at 87.7 to 88.1°. It is only slightly soluble in water but miscible with most of the common organic solvents. It has a peculiar, sharp odor. Some other properties are: n_D^{20} 1.4775; d_4^{20} 0.9891; M_R calcd., 24.61; M_R found, 25.30.

Anal. Calcd. for C_4H_3Cl : C, 54.23; H, 5.64; Cl, 40.11. Found: C, 55.04, 55.11; H, 5.70, 5.90; Cl, 39.75, 40.03.

Its chlorine atom is exceedingly reactive. When mixed with alcoholic silver nitrate it rapidly yields a copious precipitate of silver chloride. This fact in itself indicates that the compound is not a 1,3-diene, since in such a structure the chlorine atom would, of necessity, be attached to a doubly bonded carbon. Furthermore, the compound does not react with maleic anhydride or with naphthoquinone. It is not a true acetylenic compound either since it does not yield any derivative with ammoniacal cuprous chloride. When treated with ozone it yields formaldehyde and (after oxidation with potassium permanganate) chloroacetic acid. The compound has also been directly oxidized with potassium permanganate. The only product obtained was chloroacetic acid. Acetic acid and oxalic acid were absent. This behavior demonstrates the presence of the groups $CH_2=$ and $=CH-CH_2Cl$, and the compound must therefore have the structure chloro-4-butadiene-1,2. This structure is further confirmed by the fact that under the action of cold concentrated sulfuric acid, chloro-4-butadiene-1,2 is readily converted into chloro-4-butanone-2.²

² Cf. Gustavson and Demjanoff, *J. prakt. Chem.*, [2] 38, 201 (1888); Bouis, *Ann. chim.*, [10] 9, 402 (1928).

The transformation of chloro-4-butadiene-1,2 into chloroprene exemplifies a type of reaction that is common to many substituted allyl halides. Such halides (e. g., $\text{CH}_3\text{CHXCH}=\text{CH}_2$ or $\text{CH}_3\text{CH}=\text{CHCH}_2\text{X}$) arise quite generally by the addition of halogens or hydrogen halides to 1,3-dienes, and in these cases the possibility of isomerization frequently makes it difficult or impossible to determine whether the primary product is the result of 1,2 or 1,4 addition. Chloro-4-butadiene-1,2, however, differs from other allyl halides: the α,γ shift brings the adjacent double bonds into the more stable conjugated configuration and the chlorine atom becomes attached to a doubly bonded carbon where its mobility is lost. A reversal of the isomerization is therefore impossible, and chloro-4-butadiene-1,2 cannot be other than a primary product of the addition of hydrogen chloride to vinylacetylene.

The transformation of chloro-4-butadiene-1,2 into chloroprene has been observed under a variety of conditions: by the action of powdered potassium hydroxide, by the action of hot quinoline (140–150°), by the action of heat (290°) in the presence of silica gel, and by the action of hot dilute hydrochloric acid.³ However, the isomerization occurred most smoothly and rapidly in the presence of hydrochloric acid containing cuprous chloride. Fifty grams of chloro-4-butadiene-1,2 was refluxed for three and one-half hours with 20 g. of cuprous chloride in 100 cc. of 18% hydrochloric acid. The oily layer was decanted, dried and distilled. The entire specimen except for a small amount of undistillable residue came over between 59 and 63° and the distillate was pure chloroprene. When the chloro-4-butadiene-1,2 was similarly treated with aqueous cuprous chloride alone it was recovered unchanged.

Chloro-4-butadiene-1,2 unlike its isomer chloroprene shows no tendency to polymerize. It can be distilled unchanged at ordinary pressure, and specimens stored under the ordinary laboratory conditions for many months remain unaltered. It undergoes no change even when submitted to a pressure of 6000 atmospheres for forty-five hours at 50°.⁴

Experimental Part

Oxidation of Chloro-4-butadiene-1,2.—To a mixture of 30 g. of chloro-4-butadiene-1,2 with 250 cc. of water containing a little sodium carbonate was added in small portions with constant stirring 214 g. of potassium permanganate. The mixture was filtered, the filtrate acidified and continuously extracted with ether for several hours. The ether solution on distillation gave a liquid boiling at 185° which solidified on cooling. This was chloroacetic acid, identified by its melting point, neutralization equivalent (found, 96; calcd., 94.5) and transformation into chloroacetamide, m. p. 119°. No acetic or oxalic acid was found.

Ozonization of Chloro-4-butadiene-1,2.—A solution of 20 g. of chloro-4-butadiene-1,2 in 20 cc. of chloroform was treated with ozone for twelve hours at 0°. The

³ We are indebted to Dr. D. D. Coffman for some of these observations.

⁴ We are indebted to Dr. H. W. Starkweather for this observation.

solvent and the unchanged material were evaporated *in vacuo* and the remaining ozonide was decomposed with water. Formaldehyde was detected in the aqueous solution by its strong odor and the formation of methylene-di- β -naphthol; white needles melting at 204° (corr.).

Chloroacetaldehyde was not detected directly. The aqueous solution was treated gradually with 50 g. of potassium permanganate, the excess permanganate destroyed with sulfur dioxide, and the filtrate extracted with ether. Distillation of the ether solution left a residue which crystallized on cooling. This product was chloroacetic acid, identified by its melting point and neutralization equivalent.

Hydration of Chloro-4-butadiene-1,2.—Into 250 cc. of concentrated sulfuric acid 88.5 g. of chloro-4-butadiene-1,2 was added dropwise with stirring, the temperature being maintained at -5 to 3°. The dark reaction product was poured onto cracked ice, partly neutralized with sodium carbonate and extracted with ether. The ethereal solution was washed, dried and distilled, yielding 58 g. of crude chloro-4-butanone-2, b. p. 110–123°. On redistillation it boiled at 120 to 122° at 760 mm.

Anal. Calcd. for C_4H_7OCl : C, 45.07; H, 6.57; Cl, 33.33. Found: C, 45.42, 45.42; H, 6.81, 6.47; Cl, 32.26, 32.42.

When treated with phenylhydrazine it gave a derivative having the correct melting point (77°) and analysis for phenylmethylpyrazoline.⁵

Anal. Calcd. for $C_{10}H_{13}N_2$: C, 75.00; H, 7.50; N, 17.50. Found: C, 74.32; H, 7.60; N, 17.10.

Dichloro-2,4-butene-2.—This material is obtained as a by-product in the preparation of chloroprene and it is readily prepared in quantity by shaking vinylacetylene with an excess (4 moles) of hydrochloric acid containing cuprous chloride. It is a colorless liquid having a characteristic odor; other properties are: boiling point 127–129° at 756 mm., 61–63° at 70 mm., 53 to 54° at 50 mm., d_4^{20} 1.1591, n_D^{20} 1.47239, n_C^{20} 1.46988, n_F^{20} 1.48187, M_R calcd. 29.94, M_R found 30.27.

Anal. Calcd. for $C_4H_6Cl_2$: C, 38.40; H, 4.80; Cl, 56.80. Found: C, 38.53; H, 4.87; Cl, 56.90.

The proof of the structure of this compound will be presented in a future paper dealing with its reactions.

Acknowledgment.—The writers are indebted to Mr. O. R. Kreimeier for assistance in the experiments on the addition of hydrogen chloride to vinylacetylene.

Summary

The results of experiments on the action of aqueous hydrogen chloride on vinylacetylene are described. The initial step consists in 1,4 addition and the primary product is chloro-4-butadiene-1,2. This readily undergoes isomerization, yielding chloroprene, which always constitutes a part of the reaction product. When cuprous chloride is present in the reaction mixture the isomerization proceeds more rapidly and no chloro-4-butadiene-1,2 is found in the reaction product. When sufficient hydrogen chloride is present the reaction proceeds further, yielding dichloro-2,4-butene-2.

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⁵ Maire, *Bull. soc. chim.*, [4] 3, 272 (1908).

Compression Stress Strain of Rubber

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By inflating a hollow thin-walled sphere of rubber, it is possible to determine stress-strain curve without resort to actual compression. Difficulties and errors inherent in direct compression tests are avoided. The method depends on the relation existing between a compressive force and the tensiles employed in two-dimensional stretching that would effect the same deformation in the rubber as the compressive force. The method assumes negligible volume change in the rubber.

The inflation of a hollow sphere is a convenient way of applying under accurate controls the tensiles for two-dimensional stretching. The experimental quantities determined on the inflating sphere are gas pressure and dimensional measurements. Typical results on cold-cured pure-gum balloon stock are cited, including breaking point of the compression curve, energy of compression, and hysteresis.

Data for compression and for ordinary one-dimensional extension strongly indicate that these two operations are continuous, and that the stress-strain curves for the two constitute a single continuous curve. Based on such continuity being a fact, the main features of the complete stress-strain curve for rubber are described. Stress conditions at a point in deformed rubber are discussed, and attention is drawn to the analogy with pressure at a point in a fluid.

THE physics and the physical testing of rubber have received much attention. This naturally has centered in the property for which vulcanized rubber is notable among materials—its high elastic deformability. For the most part, this property has been studied through stretching

tests by extending the specimen in one direction and diminishing it in the two transverse directions.

Much less attention has been given to the compression characteristics. The reason probably lies more in the difficulties of carrying out a compression test than in less importance attaching to compression phenomena. Mechanical rubber goods, such as automobile rubber shackles, universal joints, and shock absorbers on railway coaches, are regarded conventionally as proper subjects for compression studies. That, in actual service, compression plays a prominent part hardly needs to be emphasized. Tire treads, inner tubes, and rubber heels and soles are among stocks used in large volume which are subjected to compression in service or which undergo the one-dimensional decrease and two-dimensional increase in size, characteristic of compression. Indeed we may regard this sort of deformation as decidedly more common in the usage of rubber goods than the one-dimensional increase and two-dimensional decrease in size employed in the more usual stretching tests.

Although the importance of the compression stress strain is obvious, its accurate determination over its entire course has presented formidable difficulties which no doubt have retarded progress. These difficulties reside in the frictional forces which develop between the faces of the rubber and the compressing surfaces, and in nonuniform deformation of the rubber specimen. The former prevent one from knowing what force is expended on the compression itself, and the latter means that the *sine qua non* of any determination of stress and strain relationship is wanting. Errors arising from these sources become greater as the degree of compression increases.

Birkitt (4) reviews work on the compression characteristics of rubber down to 1925. The early studies of Clapeyron (3) and of Lundal were concerned with volume compressibility as distinct from alteration of shape under compression (with volume substantially constant), which is the sense in which "compression" is used in the present paper. Later Boileau, Heinzerling and Pahl, Stévant, Breuil (6), and Van Heurn studied compressibility as we understand it here. They used machines by means of which the test specimen was compressed between parallel plates. Birkitt (4) used such a machine and reported analogies between the elongation-stress and the compression-stress curves. In a later paper Birkitt and Drakeley (5) showed that more consistent results are obtained by lubricating the rubber-metal interface, petrolatum being preferred.

Hippensteel (10) described tests on the cutting resistance of rubber insulation, which he subsequently (11) pointed out could be adapted to compression tests of a more general nature. His machine was used later by Ingmanson and Gray (12) in a study of compression and shear resistance of rubber stocks. They showed the marked effect of lubrication of the

rubber-metal surface. Abbott studied resistance to flexure under compression (1) and described a "compressetometer" for making compression tests (2). Church (7) studied the compression stress strain of sponge rubber. Ariano (3), pressing molded cylinders of rubber between parallel plates, obtained compression stress strains up to 55 per cent compression. The latter author also has made an elaborate mathematical analysis of the compression stress strain. Recently Jacobs (13) and Douglas (9) have published compression results obtained by the parallel plate method, apparently without lubricant; the work of Douglas bears more particularly on compressions at low temperatures.

We may summarize this previous work on the compression characteristics of rubber by saying that it has comprised (1) tests of a practical type which apparently did not aim at establishing a pure compression-stress relationship, and (2) tests having such a relationship as their objective, and that in the latter class of tests the technic has been that of directly compressing the specimen between parallel plates, either with or without the aid of a lubricant. We may conclude also that, where a lubricant has been used, it has alleviated the difficulties of direct compression mentioned above but has not removed those difficulties or the error resulting from them.

It is the purpose of the present paper to outline a method of determining the compression stress strain of rubber which is free from error due to friction or to nonuniform deformation. The method is an indirect one and consists of substituting for a compressive force two transverse stretching forces and of calculating from these what the corresponding compressive force would have to be in order to cause the same degree of shortening in one direction. The method of the present authors does contain the possibility of error from another source—namely, neglect of such volume change as may occur in large deformations—though it is not the intention herein to treat in detail of this source of error. Before discussing how best to apply tensile forces so as to bring about two-dimensional stretching, the relation existing between such tensile forces and the equivalent compressive force will be shown.

COMPRESSIVE FORCE AS FUNCTION OF STRETCHING FORCES

Suppose, as in Figure 1, that we have a cube of unstressed rubber, A , of unit length. Let this be compressed so that it assumes the shape B , in which the height of the specimen has been diminished to the distance, y , which is less than unity. Let the new value for each of the two lateral dimensions be x . Then x will be greater than unity and, assuming that the volume of the rubber has not changed, will be equal to $y^{-1/2}$.

It is clear that, in so far as the application of external forces to the specimen is concerned, there are two ways in

which this deformation can be effected. One is to compress the specimen by applying a compressive force in the vertical direction; the other is to apply two tensile forces perpendicular to each other and also perpendicular to the direction of compression in the first case. Obviously, when mutually perpendicular tensiles are applied, they stretch the specimen in the two lateral directions and diminish it in the third; and, if one gives appropriate values to these tensiles, they can be made to bring about exactly the same change in shape as a single compressive force (any volume change being neglected).

Now a given deformation in a given specimen of rubber is effected by doing a given amount of work on the rubber. The work done, partly expended on overcoming internal friction in the rubber but mostly stored as potential energy, is independent of whether the external forces are tensions or compressions (its amount depends only on the degree of deformation). The work done to change the unstrained cube, *A*, to the strained cuboid, *B*, is the same whether the rubber has actually been compressed in one direction or whether it has

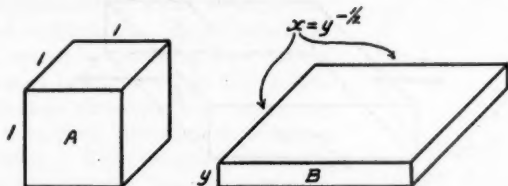


FIGURE 1. UNSTRESSED RUBBER CUBE AND STRAINED RUBBER CUBOID

actually been stretched in two directions. The same principle holds for the work done to impress an additional strain on an already strained specimen—the amount of additional work depends on the magnitude of the strain increment and is independent of the nature of the impressing forces. This principle enables the relationship between compressive force and the equivalent tensile forces to be determined.

Suppose the strained specimen, *B*, is under the compressive force, *P*. Let it be compressed through the further small distance, *dy*. The small increment of work is

$$dW = Pdy \quad (1)$$

Again, considering the strained specimen, *B*, let the compressive force, *P*, be replaced by two tensile forces, *T*, which are perpendicular to each other and to *P*. Let the forces, *T*, be of such magnitude that they maintain the shape of the specimen as it was when compressed by *P*. Now let *T* be slightly increased so as to bring about the same increment of strain as in the former case—that is, so as to diminish *y* by *dy*, or so as to increase *x* by *dx*. Then the increment of work done on one of the two lateral faces that are moved by a force is

$$dW' = Tdx$$

and the work done on both faces which move simultaneously under a force is

$$2dW' = 2Tdx \quad (2)$$

But since the work done by the first method of increasing the deformation is equal to that done by the second,

$$\begin{aligned} Pdy &= 2Tdx \\ x &= y^{-1/2} \end{aligned} \quad (3)$$

Since

$$dx = -\frac{x^2 dy}{2}$$

Therefore

$$Pdy = 2T\left(-\frac{x^2 dy}{2}\right)$$

$$P = -x^2 T \quad (4)$$

$$P = -y^{-1/2} T \quad (5)$$

Equation 4 defines the compressive force as a function of the equivalent tensile and of the new (diminished) length in the direction of compression when the original (unstrained) specimen is a cube of unit length; Equation 5 defines the

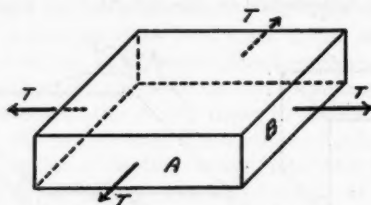


FIGURE 2. SLAB OF RUBBER STRETCHED IN TWO DIRECTIONS

compressive force in terms of the equivalent tensile and of the new (augmented) length in the directions of expansion. It should be emphasized that P and T do not both act at any one time on the specimen; they are the alternative forces, either of which may be employed to get the same result as far as degree of deformation of the specimen is concerned, and they are called "equivalent" in the sense of their equal effects on deformation.

In computing the compression stress-strain data from measurements of tensiles in two directions, it may be more convenient to measure the expanded lengths, x , and to calculate the diminished length, y , than to measure the latter directly. If so, from Equation 3 we obtain:

$$y = x^{-2} \quad (6)$$

P and y are the quantities which, for various degrees of compression on a specimen, constitute the compression stress-strain data. Either Equation 4 or 5, therefore, may be used to compute P , and Equation 6 to compute y from measurements on a two-dimensional stretching operation which involves no direct measurements of compressive force, and which in fact does not subject the specimen to actual

compression. The negative sign in Equation 4 or 5 arises from the circumstance that P is a pressure and T a tensile, and means that these forces are exerted in opposite directions as regards the specimen; P is directed toward and T away from the specimen.

HOLLOW SPHERE AS TEST SPECIMEN

We must now consider how we may apply tensiles in a two-way stretching operation, and do so without encountering difficulties as great as those associated with actual compression. The question is: How shall we apply tensile forces in two mutually perpendicular directions, have them act uniformly over the faces to which they are applied, and accommodate themselves to the continuously changing shape of those faces? As a slab of rubber is stretched in two directions (Figure 2), the faces A and B , across which the tensiles act, become longer and narrower; it is clear that the difficulties become greater as the degree of extension increases.

Prache (14) tried various expedients to overcome the obvious difficulties which arise when a flat sheet is employed as specimen. He did not, however, succeed in showing how such a sheet may be subjected to high extension in two directions simultaneously with a uniform distribution of stress and strain. While Prache had the determination of the two-way extension stress strain in mind (as distinct from the present purpose of computing the compression stress strain from measurements on two-way extensions), nevertheless it is obvious that, as a step in computing the latter relationship, the method of stretching a plane slab in two directions simultaneously can be no more accurate than it is as a direct measure of the former relationship.

What is necessary, in order that the P - T relation of Equation 4 or 5 may be used, is a technic that will permit of the following: (1) stretching of a portion at least of a sample of rubber uniformly in two directions up to the breaking point with uniform distribution of tensile force over the progressively changing faces; (2) convenient measurement of tensiles and elongations. The inflation of a hollow sphere of rubber having a thin and uniform wall fulfils this requirement perfectly. The wall of such a sphere comes under a two-way tension when the sphere is distended with gas pressure.

If, as in Figure 3, we have a distended hollow sphere of radius, r , filled with gas under a (differential) pressure, G , the total force borne by the wall across a circumference is $\pi r^2 G$. But we wish to know how much of this force is borne by that area in the cross section of the wall of the distended sphere which had unit area originally (before distension), for this is

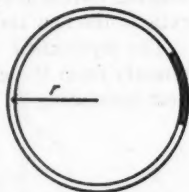


FIGURE 3. DISTENDED HOLLOW SPHERE OF RUBBER

the tensile, T , of Equation 4 or 5. The original cross-sectional area presented by the wall of the sphere is $2\pi rm/x$, where m is original wall thickness and x has the meaning heretofore used—namely, the length to which a unit length increases when the specimen is extended two-dimensionally. From the foregoing,

$$T = \frac{\pi r^2 G}{2\pi rm} = \frac{rGx}{2m} \quad (7)$$

From Equation 7 it is clear that we may follow the tensile forces in the wall of the sphere, as the latter is distended, by measuring the original wall thickness, m , which is a constant for a given sphere, and taking readings at intervals on the variables r , G , and x . In the experimental trial of the method, x was determined by making a mark on the undistended wall of the sphere 1 inch (2.54 cm.) long and by measuring this at each degree of extension. Of course, in place of this, the original radius of the sphere can be measured, whereupon the ratio of the new radius to the original radius is the quantity x .

The equivalent compressive force, P , may be calculated directly from the experimental data, r , G , x , and m , without first calculating T , by combining Equations 4 and 7 thus:

$$P = - \frac{rGx^4}{2m} \quad (8)$$

EXPERIMENTAL PROCEDURE

In the experimental trial of these principles, rubber balloons¹ have been used since they afford a fair approximation to the spherical shape required in theory. The balloons were the usual cold-cured type; undistended they were about 5 cm. in diameter and their walls were about 0.03 to 0.04 cm. thick.

BALLOON INFLATION. Figure 4 shows the arrangement by which the balloon was distended and by which readings were taken. The neck of the balloon, B , is taped securely to a glass tube, T ; the latter leads, through a three-way stopcock, SC , to an air inlet, A , and to a manometer, M . The balloons tend to be pear-shaped; but this deviation from the spherical was minimized by taping down most of the neck region.

Before a balloon was fastened to the tube, two bench marks (one vertical and one horizontal) were made in the equatorial region as shown in Figure 4. These marks were 1 inch (2.54 cm.) long and were the means by which the expansion of the balloon was followed. The thickness of the wall in the bench-marked region prior to inflation was determined on a Randall and Stickney gage by measuring the folded stock and dividing the reading by two. The equatorial part was chosen as the place in which to observe the stress-strain properties because it was found most uniform in thickness; in particular, the pole opposite the neck was rejected on account of less

¹ Balloons were supplied by the Eagle Rubber Company, Ashland, Ohio.

consistent thickness and shape. It was considered better practice to take readings on a small area, marked as just described, than to consider the entire balloon as the test specimen. By confining readings to a small and well-chosen area, such variability in thickness and such imperfect sphericity as a balloon exhibited were made of less moment.

The liquid used in the manometer was a sulfuric acid solution of about 1.66 density; this was checked before each inflation experiment, in view of minor changes in density which occurred from day to day.

Each inflation was carried out according to a predetermined schedule. The schedules used on various balloons were such as to cause diminution of wall thickness at one or the other of the following rates, approximately:

- 0.0013 cm. (0.0005 inch) per minute
- 0.0025 cm. (0.001 inch) per minute
- 0.0076 cm. (0.003 inch) per minute
- 10 per cent of the actual (remaining) thickness per minute
- 20 per cent of the actual (remaining) thickness per minute
- 40 per cent of the actual (remaining) thickness per minute

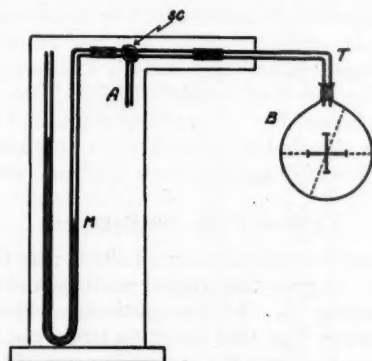


FIGURE 4. ARRANGEMENT FOR DISTENTION OF BALLOON

The increments which the one-inch bench marks would have to show at fixed time intervals, in order that wall thickness should diminish at each of these rates, were calculated and the dilations were conducted accordingly.

In inflating a balloon, air was introduced at intervals of one minute. It was found more convenient to blow in air from the lungs than to use compressed air. With the stopcock turned so as to connect the balloon with tube A, air was introduced until the bench mark had increased as demanded by the inflation schedule for the balloon in question. Then the stopcock was turned so as to connect the balloon with the manometer, and the difference in height of the manometer arms was read. This difference in centimeters multiplied by the density of the manometer liquid yields the gas pressure values, G . At the same time, the bench marks and the circumference of the balloon in two directions were measured. The average of the two readings on the bench marks yields the quantity x , and the radius calculated from the

average of the two circumference readings is the radius r of Equation 8. Of the circumference measurements, one was taken equatorially, the other almost vertically, but missing the immediate vicinity of the neck (as shown by the dotted lines in Figure 4). A balloon required altogether from 5 to 70 minutes for inflation, depending on the rate.

BALLOON DEFLATION. In the case of several balloons after they had been inflated nearly to the breaking point deflation data were taken in order to learn something of the hysteresis of the compression stress strain. The procedure used for inflation was followed, except that air was released a little at a time through the stopcock, measurements being taken on the pressure and on the bench marks at each step. The deflations were accomplished in much shorter time than the inflations, about 2 or 3 minutes being allowed for the air pressure to subside.

ONE-WAY EXTENSION TESTS. An object was to compare the ordinary stress strain for elongation (one-way extension) with that for compression. To obtain the former, dumb-bell shaped specimens were cut from several unstretched balloons. These were gaged for thickness and were bench-marked in the usual way. In order to make the rate of extension low (roughly comparable with the balloon dilations), the strips were tested by the dead weight method. One end of the specimen was fastened in a supporting clamp, and to the other end a pan was attached to which weights were added so as to give an extension of roughly 0.1 inch (0.25 cm.) per minute.

TYPICAL DATA ON BALLOON

Table I shows how the data for a balloon may be tabulated conveniently. It gives the original readings and the derived values for balloon 13. As this particular balloon was distended at a rather high rate, its stress strain was determined by fewer points than was the case with some of the balloons tested. This example, however, illustrates quite well how the compression stress strain data are derived in a particular case from the quantities measured on the expanding sphere.

The gas pressures as measured by the manometer for each step of the inflation are shown in column G . The radii in column r correspond with the mean values for the equatorial and horizontal circumferences shown in the two preceding columns. The values of x are the means of the horizontal and vertical elongated bench-mark readings of the two preceding columns. The three variables, G , r , and x , together with m (the original thickness of the balloon wall), furnish, through Equation 8, the values of equivalent compressive force P which occur in the next column. The values of y , the compressed thickness of what was a unit thickness before compression (given in the next column), are obtained from the x column through Equation 6. The P and y columns constitute the compression stress-strain data which it is the object to deduce. In the last column of the table the compression is

TABLE I. ORIGINAL AND DERIVED VALUES FOR INFLATION OF BALLOON 13
 (Original wall thickness $m = 0.0305$ cm. Expansion in early part of inflation conducted so as to diminish wall thickness by about 0.00762 cm. per minute; later part of inflation involved faster rate)

GAS PRESSURE, G Grams/cm. ²	CIRCUMFERENCE Equatorial Cm.	CIRCUMFERENCE Vertical Cm.	Radius, r Cm.	—ELONGATED-UNIT BENCH MARK—		CALCD. EQUIV. COMPRESSIVE FORCE, P Kg./cm. ²	CALCD. COMPRESSED THICKNESS OF ORIGINAL UNIT THICKNESS, y	COMPRESSION %
				Horizontal	Vertical			
0	22.1	...	3.61	1.00	1.00	0	1.00	0
35.0	30.6	32.2	3.05	1.16	1.20	3.91	0.715	28.5
32.2	30.6	32.2	3.05	1.45	1.45	16.4	0.416	86.4
27.0	38.1	38.1	6.06	2.00	2.10	47.4	0.238	76.2
17.0	48.3	48.3	15.1	3.00	3.40	218.0	0.0934	96.1
14.0	92.3	92.3	15.1	4.00	4.00	504.0	0.0302	97.0
16.0	101.5	114	17.6	5.50	6.00	917.0	0.0257	97.4
18.7	117	130	19.6	6.00	6.50			

expressed as a percentage, this being analogous to the way elongation is expressed in the ordinary extension stress strain of rubber. For example, 58.4 per cent compression means that a specimen originally 1 cm. thick has lost 58.4 per cent of 1 cm. (or 0.584 cm.); it therefore still retains a thickness of 0.416 cm. (as shown in the y column). Per cent compression has been used in plotting results in order to preserve the analogy with the conventional method of expressing elongations.

Table I shows that the rubber, before it broke, diminished in one direction to the extent of over 97 per cent of its original dimension. Perhaps this figure is in error, owing to the volume of the rubber actually increasing under tension, contrary to the authors' basic assumption. Even allowing for some error from volume increase, the result seems noteworthy, especially as 100 per cent compression corresponds with complete annihilation of the dimension in question. The calculated value for the force, P , which, if it had been applied as a pressure to a 1-cm. cube of the rubber, would have been required to compress the specimen to a residual thickness of 0.0257 cm. and to rupture it at that thickness, is the seemingly high figure of 9170 kg. In English units this corresponds to a breaking compressive force of about 130,000 pounds per square inch of original cross section. When, however, one considers how greatly the area is expanded over which this force applies (thirty-nine times the original cross section for 97.4 per cent compression), the compressive force does not seem unduly great.

The P and y columns in Table I show that P increases slowly at first, reaching only 47.4 kg. per square centimeter for a compression of 76.2 per cent. Toward the end of the compression, however, P increases very rapidly—so much so as to go from 5040 to 9170 kg. per square centimeter when the compression increases from 97.0 to 97.4 per cent. It is obvious that the results for the entire compression cannot be graphed advantageously on an equal division scale for stress. To display the compression data for the entire deformation graphically, one may break the curve into parts and use a suitable scale for each part. If one resorts to this expedient, the data must be broken into about four parts, and a separate graph for each must be made. It is better for most purposes to graph the stress logarithmically; even so, it is advisable to graph the early and later part of the stress strain with different scales, so rapidly do the last few stress readings advance with increased compression.

The last point is illustrated by Figure 5 in which the stress-strain data of Table I are plotted. In this and all other graphs of compression data, the lower left-hand quadrant has been used; that is, compressive force P increases from top to bottom of the graph, and per cent compression increases from right to left. This is strictly analogous to the use of the upper right-hand quadrant for plotting the ordinary elongation stress strain, when we consider that a pressure is a

negative tension and a compression is a negative elongation. The convenience of this practice, especially when, as in the present case, an object is to correlate the elongation and compression curves as a single entity, will appear more definitely later.

The long curve in Figure 5 plots all the P -per cent compression determinations as displayed in Table I for balloon 13, the P scale being logarithmic. The short curve repeats the later part of the stress strain, affording a more advantageous display by use of a more open scale for compression.

For each balloon tested, the determined points have been plotted and smooth curves drawn through them as in Figure 5. This affords an idea of the variance in the data for a given balloon, and the smooth curve enables corrected values to be read. In the case of balloon 13 the determined points are too far apart to afford corrections. Figure 6 plots the results for balloon 17 and is shown in order to illustrate a case involving more numerous points of determination. The deviation of the points from the smooth curve in this case is typical of tests where enough points were obtained to yield corrections. At the low-deformation end of the curve the points deviate from the smooth curve quite appreciably. This was generally true and perhaps followed from the technic involving higher relative errors in the measurement of the bench marks at low extensions. At any rate, the "zero end" of the compression stress strain cannot be considered very accurately delineated.

Balloon 17, as graphed in Figure 6, and several other balloons for which the data approach the zero end fairly closely, are of interest, however, in giving an indication at least of the course of the curve for small deformations—a matter of importance in attempting to correlate the compression and elongation stress strains. Balloon 17 was not distended to a break. It was inflated to a calculated compression of 97.0 per cent and a calculated compressive force of 5180 kg. per square centimeter which undoubtedly was close to rupture. At this stage, however, the balloon was deflated to obtain the hysteresis curve, and the latter likewise is shown in Figure 6.

RESULTS NOT INFLUENCED BY RATE OF COMPRESSION

Before starting the work, it was considered possible that the modulus of the compression stress strain and perhaps the

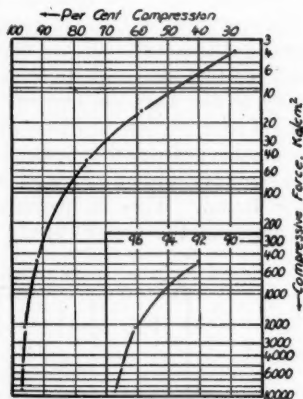


FIGURE 5. STRESS-STRAIN DATA OF TABLE I (BALLOON 13)

end point would be influenced by the rate of deformation. Provision was therefore made for tests of various rates as previously defined. The results, however, do not disclose any influence of rate of compression. This is made clear by Table II in which moduli on each of nine balloons, compressed at various rates, are shown. These moduli, or compressive forces for given degrees of compression, show as much divergence between two balloons tested at a given rate as they show between one rate and another. It is evident that the variability of the balloons exceeds any influence which variable rate of compression may have entailed. This is borne out also by ordinary elongation tests on the stock of other balloons of the same lot, among which an equal, if not greater, variability was found. This is perhaps to be expected. For the purposes of the present study it has been deemed sufficient,

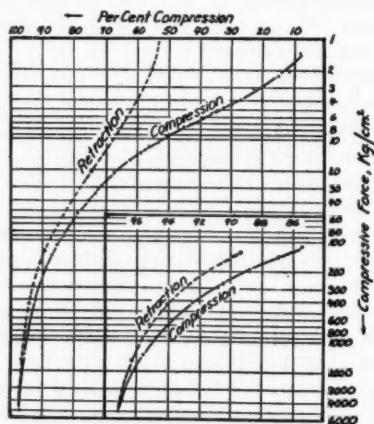


FIGURE 6. STRESS-STRAIN DATA FOR BALLOON 17

therefore, to base conclusions of a general nature on the approximate mean results of Table II.

The moduli of Table II are the corrected values obtained by reading from smooth curves similar to Figures 5 and 6 drawn through the original data. It is not inferred that greater changes in the rate of deformation than have been here employed would not have influenced the compression results. Such an influence, comparable with that which exists when rubber is elongated in one direction at various rates, is almost certain to exist for compressions (or for two-directional elongations) also, if the rate be sufficiently varied.

BREAKING-COMPRESSION DATA

Of the nine balloons summarized in Table II, only two were distended to rupture; the others were permitted to retract in order to obtain hysteresis data. No very accurate conclusions as to numerical values are justified from the data, particularly

TABLE II. SUMMARY OF COMPRESSION STRESS-STRAIN AND END-POINT DATA

BALLOON	APPROX. RATE OF COMPRESSION PER MIN.	COMPRESSION MODULI			HIGHEST VALUES OBTAINED ON:		BROKEN?
		P_{30}^a	K_0	P_0	Compressive force	Compression %	
16	0.00127 cm.	4.58	16.4	276	4950	96.9	No
17	0.00127 cm.	4.31	14.5	240	5180	97.0	No
21	0.00254 cm.	4.11	14.5	230	3050	96.8	No
13	0.00762 cm.	4.17	16.7	277	9170	97.4	Yes
14	0.00762 cm.	3.99	14.6	235	5650	97.3	Yes
15	0.00762 cm.	4.93	15.4	249	6260	97.2	No
18	10%	..	17.3	280	4390	96.8	No
19	20%	..	16.3	245	2675	96.6	No
20	40%	..	14.4	242	3470	97.0	No

^a P_{30} means compressive force at 30% compression on original cross section.

as to the breaking force. The breaking compression is indicated, with rather small variance, as about 97.3 to 97.4 per cent. The breaking force, however, is subject to marked variance, which is easily understood when the extreme slope of the stress-strain curve at high compressions is recalled. The breaking compressive force on this particular stock (a pure-gum cold-cured stock) may be taken as in the neighborhood of 6000 to 9000 kg. per square centimeter. It is probably not possible to obtain even rough approximations of the breaking point on compression by a technic involving actual compression of the specimen, for the latter is almost sure to be ruptured at some point prematurely by the ununiform stress which is engendered.

ENERGY OF COMPRESSION STRESS STRAIN AND HYSTERESIS LOSS

The energy of compression has been calculated for three balloons. The corrected stress-strain data, as read from smooth curves similar to those in Figures 5 and 6, were used as the basis. The corrected data were replotted on equal-division graph paper so as to permit of energy being computed by measuring the area between the stress-strain curve and the strain axis. It was necessary, as mentioned previously, to divide the graph into several parts. The authors found it desirable to make four such divisions with scales as shown in Figure 7, which plots the compression data for balloon 16. The four curves in solid line together constitute the stress-strain curve for this balloon. The energy corresponding to each portion of the curve was estimated by the "counting squares" method of determining subtended area. Due account must be taken, in the case of each curve portion, of its particular scales, since the energy equivalent of a unit subtended area depends on these and varies with each portion of the curve.

The energy required to compress one cubic centimeter of the stock in question close to, but not quite up to, the breaking point is thus estimated in the case of balloon 16 as 100 kg. cm. Further estimates of the energy of compression made from the data of balloons 15 and 17 are summarized in Table III. Considering the superficially enormous compressive forces involved, these energies are not high. This, of course, is because the distance through which compression progresses under very high stress is small.

TABLE III. SUMMARY OF ENERGY OF COMPRESSION AND OF
HYSTERESIS

BALLOON	HIGHEST COMPRESSION REACHED	ENERGY OF COMPRESSION	ENERGY OF RETRACTION	HYSTERESIS LOSS	HYSTERESIS
	%	Kg. cm.	Kg. cm.	Kg. cm.	%
15	97.2	103	69	34	33
16	96.9	100	71	29	29
17	97.0	89	58	31	35

When the ordinary (one-way) elongation stress strain of stock from the same lot of balloons was determined by the

dead weight method, as previously described, the energy capacity up to the breaking point ranged from 50 to 70 kg. cm. per cubic centimeter. In view of the higher energy figures obtained on compression than on elongation, and in view of the fact that the former does not include and the latter does include the breaking point, it would appear that the capacity of this stock to absorb energy on being compressed to rupture exceeds its capacity on being stretched to rupture. Whether this is a general rule or not is not known, but it is at least indicated that compression may permit of more energy absorption than does elongation. However, it would appear that the two energies are of the same order of magnitude.

We may well consider that energy is about the best common measuring stick to apply to both compression and extension deformations. A compression is not equivalent to an extension in any sense of the word when each involves the same stress or the same actual or relative change in any given dimension. Yet in a significant sense, a compression is equivalent

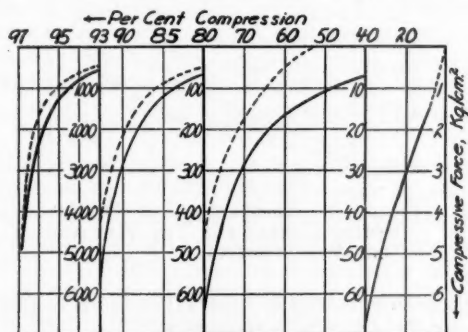


FIGURE 7. COMPRESSION DATA FOR BALLOON 16

lent to an extension on a unit volume of elastically deformable matter if equal amounts of work have been done to bring them about. From this standpoint, therefore, the stock of the balloons tested may be regarded as capable of withstanding more severe deformation when the change is a shortening in one direction and a lengthening in the other two than when it is an elongation in the one direction and a contraction in the other two.

This view is supported by elongation data for both types of deformation. In the usual type of one-dimensional extension, the breaking elongations on five test pieces ranged from 640 to 710 per cent. The two-dimensional elongations, on the other hand, on balloons 13 and 14 which were distended to rupture were 525 and 505 per cent, respectively. That these two-dimensional elongations imply a greater degree of strain than is implied by the superficially greater one-dimensional elongation is clear when one recalls what is involved. In the case of stretching balloon 13, for instance, what has

occurred amounts to this: A cube of rubber 1 cm. long has been stretched in one direction until it has elongated by 5.25 cm.; it becomes much reduced in the other two directions. Then, while the 5.25-cm. gain one way is maintained, the specimen is pulled out along one of the reduced dimensions until that also has increased by 5.25 cm. (attained 6.25 cm.). By this second stretching at right angles to the first, the third and remaining dimension becomes further reduced, reaching, in fact, the surprisingly small value of 0.0257 cm. A consideration of this sort fortifies the idea that the two-dimensional stretching, or the equivalent compression, conducted on the balloon stock imposed a greater strain than did the one-dimensional stretching.

Figure 7 shows the retraction stress strain by broken lines. The areas between these and the solid lines for compression together constitute the hysteresis loop. The energy lost by

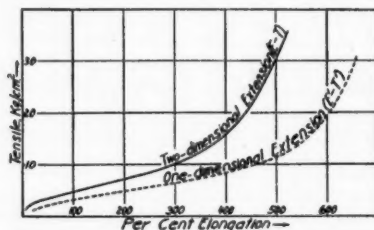


FIGURE 8. COMPARISON OF STRESS-STRAIN CURVES FOR TWO-WAY AND ONE-WAY STRETCHING

hysteresis as summarized in Table III amounts to about 30 to 35 per cent of the work of compression.

STRESS-STRAIN CURVE FOR TWO-DIMENSIONAL STRETCHING

While the present method of computing the compression properties involves stretching a specimen in two directions at once, the immediate data of that operation are in themselves of interest. These data are the elongations obtained simultaneously in the two directions together with their accompanying tensiles. Equation 7 gives the two-way tensile, T , as a function of the experimental quantities, and the two-way elongation is, of course, just another way of expressing the quantity x , for elongation equals $100(x - 1)$ per cent.

Figure 8 shows the stress-strain curve for two-way stretching superimposed by way of comparison on that for one-way stretching. The two-way values, identified by the symbols E and T , are shown by a solid line; the one-way values, identified by the symbols E' and T' , are indicated by a broken line. The $E'-T'$ line is the ordinary extension stress strain of the stock as determined by the dead weight method. The $E-T$ line represents a composite set of data based on balloons

13 and 17. Each curve is typical of the stock from the standpoint of the particular relation it depicts.

As might be expected, the E - T curve shows higher moduli than that for E' - T' . Energy of compression may, of course, be computed directly from the E - T curve, for the latter is but a different way of expressing the compression data. It should be recalled that, in computing energy of compression from the E - T curve, twice the area subtended must be taken, since two tensiles, each equal to T , are working simultaneously.

By no means are the E - T curve and the E' - T' curve two ways of expressing the same facts. They are unrelated, except empirically, as also are the ordinary elongation stress strain (the E' - T' curve) and the compression stress strain. The entirely empirical nature of any relation which may exist between these latter curves is referred to later.

COMPRESSION CURVE CONTINUOUS WITH ELONGATION CURVE

From the theoretical side it is difficult to see any reason for expecting to find a discontinuity between the compression and the one-way extension properties of rubber. If on a piece of stretched rubber the tensile is reduced, the rubber shortens. As the process continues, stress and strain follow a continuous curve. Consider the rubber when it is still subject to a small tensile and when it is just slightly stretched. If the tensile is lowered further, it may be brought to the zero point or it may attain a negative value (become a compressive force). If the tensile is carried to a small negative value, the elongation becomes slightly negative (becomes a compression). On going from a point on the extension curve in the neighborhood of the zero point to a neighboring point on the compression curve, the same change in properties is entailed as occurs when one proceeds down the extension curve toward the zero point—namely, elongation and tensile force suffer decrements in the algebraic sense. It is difficult to see in what respect any different thing is done in passing through the zero point and in passing from extension to compression, or vice versa, than is done in passing up or down either one of these curves without crossing the zero point.

These considerations have led the authors to expect that, when the compression data and the elongation data for the same vulcanizate are plotted together in analogous ways, they will produce a continuous curve. The experimental data on this are not conclusive, but they strongly support this view. In Figure 9 are plotted original data for extension and for compression in the neighborhood of the zero point. None of our determinations for either type of deformation was taken, unfortunately, as close to the zero point as might be desired in the present connection. The points in the elongation quadrant of Figure 9 are the original points determined in a representative stretching test. Those in the compression quadrant are the original points for the compression of the

stock in balloon 17. Both sets of data are chosen for display because they show more than usual detail in the neighborhood of the zero point. These data seem to furnish fair, but not quite conclusive, proof of continuity, and the authors hope to give this matter further study.

Considered somewhat more critically by plotting the points of Figure 9 on a larger scale (Figure 10), the compression points lead to a smooth curve which, on extrapolation, does not pass through the origin. It intersects the strain axis at about 0.7 kg. of compressive force. In fact, of course, the compression curve must, in the nature of things, pass through the origin; and, when our data lead to the smooth extrapolation thus somewhat avoiding the origin, there are just two possibilities. Either (1) the extrapolated part of the relation undergoes an unlikely sharp change of curvature near the origin which is quite unsupported by data and unaccounted for in theory, or (2) the entire set of compression results, near the top of the curve at least, are experimentally low on the

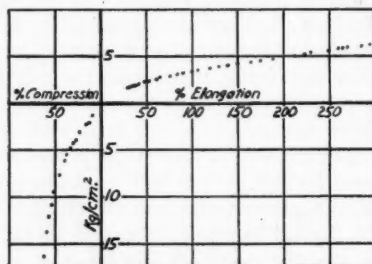


FIGURE 9. EXTENSION AND COMPRESSION NEAR ZERO POINT

graph. The latter is the more likely alternative. If the compression curve is lifted, without change in shape or direction so that its extrapolated end passes through the origin, it and the extrapolated end of the elongation curve will meet with the same slope within limits of the experimental accuracy.

The conclusion seems justified that any imperfection of the experimental data as evidence of continuity between compression and extension properties may be assigned to error. In Figure 10 the graph is on a large scale and is confined to a small region of the stress-strain results in close proximity to the origin. The data used are the same as in Figure 9. The extrapolated ends are shown in broken lines. The upper dotted curve in the compression quadrant coming away from the origin is the actual compression curve moved up to meet the origin but suffering no other change.

ANALYTIC FEATURES OF STRESS-STRAIN CURVE FOR RUBBER

If we accept the foregoing thesis of continuity of compression and extension, it alters our outlook on the much-debated

equation of the stress-strain curve for rubber. The complete curve may be regarded as having a positive (extension) branch and a negative (compression) branch. Any equation which is proposed for the curve must fit both branches; it must be one which yields all values of stress and strain encountered experimentally and not just those of positive sign.

It is beyond the scope of the present paper to attempt any discussion of the equation for the curve. We may, however, ask: What are the analytic features to which the curve conforms and which will govern its equation?

1. The curve passes through the origin with negative curvature (convex upward).
2. The part to the lower left of the origin (compression branch) passes downward with increasing slope and is bound theoretically to have the vertical line representing 100 per cent compression as an asymptote. Experimentally also the curve is found to approach this vertical line asymptotically.

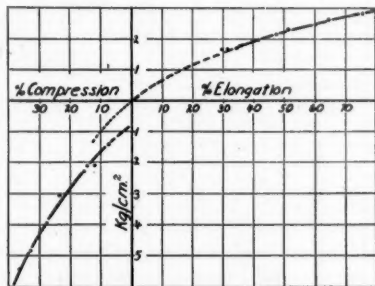


FIGURE 10. PLOT OF FIGURE 9 ON LARGER SCALE

3. It is observed empirically that in a typical case the major portion of the part of the curve above and to the right of the origin (elongation branch) possesses positive curvature (concave upward).

4. It follows from 1 and 3 that a point of inflection must exist in the elongation branch; this is usually observed experimentally and occurs in the present results at or a little before 200 per cent elongation.

5. The elongation branch in its upper part is observed empirically to approach an oblique asymptote.

In Figure 11 the complete stress strain, including compression and elongation branches, is shown. This is drawn to conform to typical results of the present study. To bring the lower end of the compression branch with its high stress into the picture, it is necessary to break the scale and curve. The solid line represents the complete stress-strain data as usually expressed—namely, with stress calculated on the original cross section of the specimen.

When stresses are calculated to the actual cross sections, we have the curve shown by the broken line. The stress for a

given strain based on the actual cross section is obtained by the well-known relation:

$$F_a = F_o \left(1 + \frac{\text{per cent elongation}}{100} \right)$$

where F_a and F_o = stresses based on actual and original cross sections, respectively.

Both branches of the stress-strain curve are elevated in the graph when stresses are based on actual as against original cross sections, and the curve passes through the origin with less curvature; this means increased values for tensile forces and decreased values for compressive forces. The apparently enormous compressive forces encountered become reduced to

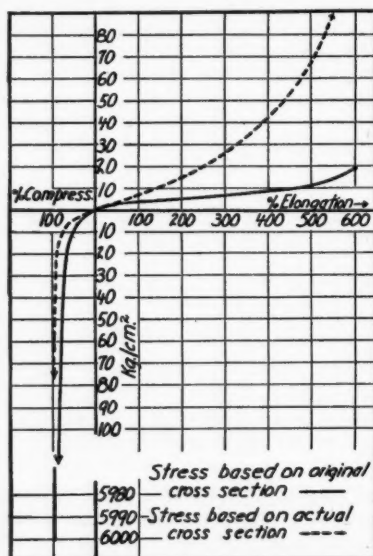


FIGURE 11. COMPLETE STRESS-STRAIN CURVE

quite reasonable size when based on actual cross section. Thus the value 9170 kg. per square centimeter, determined on balloon 13, becomes $9170 (1 - 0.974)$ kg. per square centimeter = 238 kg. per square centimeter when figured on the actual cross section.

It is of interest to note that, notwithstanding the vertical shift which the curve undergoes when stresses are changed from the basis of original to actual cross section, the analytical features described above for the former hold also for the latter.

The question of whether a point of inflection is always present in the stress strain for rubber has sometimes been discussed. If we accept continuity between compression and extension, then an inflection is an analytical necessity some-

where on the curve. It would have to exist in the compression branch, were it absent in the extension curve.

The authors believe attempts have been made to correlate the compression curve with the elongation curve on a theoretical basis, in the sense of deriving one as a mathematical function of the other. If the continuity theorem is correct, we have the following implications:

The elongation stress strain and the compression stress strain are but parts of one and the same curve.

The one will not be a function of the other in the sense of its being possible to calculate the compression stress strain from one-dimensional elongation stress-strain data, or vice versa.

On the contrary, the relationship of the compression branch to the elongation branch is entirely empirical, and it is necessary to learn the characteristics of each branch by operating on the rubber in the appropriate way—namely, by carrying out one-dimensional extensions (or two-dimensional contractions) to determine the elongation branch, and by executing one-dimensional contractions (or two-dimensional extensions) to determine the compression branch.

If it is desired to establish an equation for the stress-strain curve, this should be based on data for both the elongation and compression branches.

STRESS RELATIONS AT A POINT

While Equation 5 correlates pressure P with the equivalent tensiles, T , the true simplicity of the relation between these equivalent forces, pointed out by one of the writers (15) in a previous paper, is not manifested in Equation 5. There forces are referred to the original (undeformed) cross sections; when forces are referred to actual (deformed) cross sections, the simpler relation appears.

Retaining the symbols P and T for forces based on original cross section, and distinguishing forces based on actual cross section by P_a for compressive force and T_a for equivalent tensile forces, we may show the relationship between P_a and T_a thus:

$$P = -y^{-1/2}T \quad (5)$$

where y = diminished length after compression of what was an undeformed cube of unit length.

Since we assume the volume of the rubber has not changed on compression, the area of the face perpendicular to the dimension y (the face on which P acts) is y^{-1} . Therefore,

$$\text{compressive force on unit area} = P_a = \frac{P}{y^{-1}}$$

$$\text{or} \quad P = y^{-1}P_a \quad (9)$$

As apparent from Figure 1, the area of the face on which T acts is $y \cdot y^{-1/2} = y^{1/2}$. Therefore,

$$\text{tensile force on unit area} = T_a = \frac{T}{y^{1/2}}$$

$$\text{or} \quad T = y^{1/2}T_a \quad (10)$$

From Equations 5, 9, and 10,

$$P_s = -T^* \quad (11)$$

Since P_s and T_s are forces on unit areas of actual cross section, Equation 11 expresses stress conditions at a point. It is evident that Equation 11 applies to a deformation in which the specimen lengthens in one direction and diminishes in two directions, as well as to a shortening in one direction and lengthening in two directions for which it has been proved. The following general rule expresses the foregoing: Pressure at a point in an elastically deformed solid is numerically equal to the transverse tensions which would be capable, if substituted for the pressure, of maintaining the same strain. The analogy with the equality of pressure in all directions at a point in a fluid is striking.

FURTHER RESEARCH DESIRABLE

The authors feel that their work will have been justified if it stimulates increased interest among rubber technologists in the stress-strain relations of rubber and further study of the compression characteristics in particular. It is not their aim to lay down in this paper a cut and dried technic for determining the compression stress strain. As far as technic is concerned, the authors wish to make clear the general principles of one line of attack which undoubtedly avoids certain difficulties inherent in the commonly used method of direct compression and which seems to hold promise of being a worth while method. Regarding the stress-strain properties themselves, the aim has been to show the apparent continuity of these as between the compression branch of the curve and the more usually determined elongation branch and to emphasize that a treatment of stress-strain data which takes cognizance of such continuity and which treats of the data in their entirety is more likely to result fruitfully than a treatment which deals with the elongation branch alone.

That full development and use of the ideas presented in this paper call for further research is apparent. For example, while it is satisfactory as a first approximation to consider the volume change of rubber nil, and to base, as has been done, all formulas and calculations on that assumption, it is most desirable that attention be given to whatever effect such volume change as actually occurs may have. The immediate purpose of the investigation has been satisfied by applying the technic of distending a hollow sphere to the most readily available and convenient specimens and these, as stated previously, were cold-cured toy balloons. Before the technic can be applied to any desired composition of rubber subjected to any desired hot cure, which is where its main usefulness will lie, it is necessary to construct a mold that will enable an accurately proportioned hollow sphere of rubber to be vulcanized. Further verification of continuity between the compression stress strain and the elongation stress strain should be

obtained through a more minute experimental study of the zero ends of the two curves.

The authors purpose, as opportunity affords, to continue the study of the compression stress strain and suggest to those interested in the physics of rubber that a more intensive study of compression properties will round out the physics of rubber where it now lacks fullness and will promote the correlation of the elastic properties of rubber to ultimate structure.

SUMMARY

1. A relation of simple form between compressive force and equivalent two-way tensile forces is developed.

2. Based on this relation, a new method for determining the compression stress strain of rubber is outlined, which avoids difficulties and errors inherent in direct compression. It consists in applying tensile forces simultaneously in two directions, and, from these and the strained dimensions, in computing the compressive force that would have produced the same deformation.

3. The mode of applying the two-way tensiles is to inflate a hollow sphere of rubber; the experimental data required to determine the compression stress strain are pressure of gas in, and dimensions of, the inflating hollow sphere.

4. The method has been applied to cold-cured pure-gum rubber in the form of toy balloons which, in its ordinary elongation stress strain, shows a breaking elongation of about 650 to 700 per cent and a tensile of 30 to 40 kg. per square centimeter. While the numerical values obtained on this stock have no special significance, as they will vary from stock to stock, the following are examples: breaking compression, about 97.3 per cent; breaking compressive force, 6000 to 9000 kg. per square centimeter (on original cross section); hysteresis, 29 to 35 per cent of work of compression to near rupture.

5. As a common measuring stick by which to gage degree of strain in deformations of different types—e. g., increasing one dimension (and diminishing the other two) as against diminishing one dimension (and increasing the other two)—energy seems the best. Energy at break for ordinary elongation stress strain was 50 to 70 kg. cm. per cubic centimeter, and for compression stress strain was 89 to 103 kg. cm. per cubic centimeter.

6. The compression stress-strain data may, if desired, be expressed in terms of two-way tensiles *vs.* two-way elongations. Energy of compression may be computed either as twice the area subtended between such a curve and the strain axis, or as the area between the compression stress strain and the strain axis.

7. It is strongly indicated that the compression stress strain of rubber is continuous with the ordinary elongation stress strain when both are plotted in the same units, and that the complete stress strain should accordingly be consid-

ered as a single continuous curve having an elongation branch and a compression branch with the origin as dividing point.

8. The analytic features of the complete stress strain are described.

9. Granting the observed concavity of the upper part of the elongation stress strain, and the thesis of continuity between elongation and compression, a point of inflection is bound to exist theoretically.

10. Implications of the thesis of continuity are: (1) An equation for the stress-strain curve must fit the complete curve; it is not sufficient that it fit the elongation branch only. (2) It is impossible to compute the compression stress strain from the ordinary (one-way) elongation stress-strain data. The two sets of data are related empirically.

11. When compressive force and equivalent two-way tensiles are based on actual cross sections, stress conditions at a point are expressed and we have the simple rule: Pressure at a point is numerically equal to the transverse tensions which, substituted therefor, will maintain the same strain.

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Measuring Microscope for Rubber Specimens

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A microscope provided with a six-times micrometer eyepiece and objectives of 32 and 48 mm. focal length is suitable for measuring the cross-sectional dimensions of rubber test specimens. The width of specimens is usually greater than that of the die with which they were cut. The thickness of soft compounds as determined by the microscope is greater than that indicated by a gage of the plunger type.

A MICROSCOPE of low power, equipped with a micrometer eyepiece, affords a convenient and practical means for accurately measuring the dimensions of rubber test specimens, and at the same time permits the inspection of specimens for defects. The equipment here described was designed particularly for measuring the width of the familiar dumb-bell shaped tensile test strips. At the present time no convenient and accurate gage is available for this purpose, and it is common practice to assume that the width of the specimen is the same as the die with which it was cut. The same equipment has been found satisfactory for determining the thickness of test strips, and is generally applicable for the measurement of dimensions up to about 6.4 mm. (0.25 inch).

This use of the microscope embodies no original features. The method and equipment, however, are here described in some detail, since they may be of interest to investigators who may have occasion to make accurate mechanical measurements on rubber.

It is not the purpose of the present discussion to make a

critical comparison of dimension-measuring devices employed in connection with test specimens of rubber. Some comparative measurements are cited which indicate that the microscope affords an improvement in accuracy over existing methods, but consideration is not given here to the general subject of the probable errors in rubber testing.

THE MICROSCOPE

The microscope is of low power in order that a relatively wide field of view may be obtained. It consists of a standard microscope body fitted with a six-times micrometer eyepiece and objectives of 48 and 32 mm. focal length. With the former objective and a tube length of 160 mm., the field of view is 9.3 mm. in diameter, and the magnification 13 diameters; with the latter objective, the field is 5.4 mm. in diameter and the magnification 24 diameters. The equipment includes a mirror and a mechanical stage.

The micrometer eyepiece is a standard eyepiece on the diaphragm of which is cemented a glass disk ruled with a scale 10 mm. in length which is ruled in 100 subdivisions. The

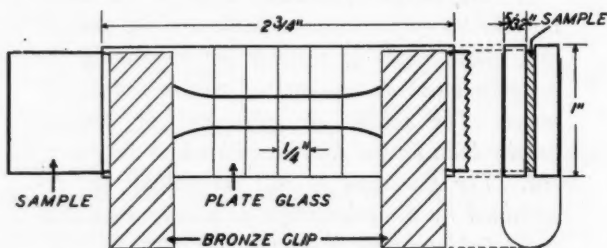


FIGURE 1. SPECIMEN HOLDER OF GLASS PLATES HELD TOGETHER WITH BRONZE CLIPS

eyepiece is provided with a focusing eye-lens in order to accommodate the micrometer scale to the eye of the observer. When an object is viewed under the microscope, the scale appears to be superimposed on it and dimensions may be read directly from the scale. A conversion factor is, of course, employed to convert the observed number of scale divisions to the desired units. The micrometer eyepiece is more convenient than a filar micrometer for work where a very high order of accuracy is not necessary, since the use of the latter requires the setting of cross-hairs on one edge of the specimen, and the moving of them to the other edge.

SPECIMEN HOLDERS

Suitable specimen holders greatly facilitate the manipulation of samples on the mechanical stage, and insure the samples lying flat without distortion. Two holders for dumb-bell shaped test strips are shown in Figures 1 and 2. One consists of two microscope slides held by spring bronze clips which are attached to the glass by de Khotinsky cement.

The clips are so adjusted that an ordinary rubber test strip is held snugly between the slides. The other holder consists of two thick glass slides near whose ends grooves are cut so that the slides with a specimen between them may be held together with rubber bands. The rubber bands do not project above the surface of the glass, since they would interfere with the free movement of the holder by the mechanical stage. Both specimen holders are so designed that measurements may be made on either side of a sample without removing it from the holder. The slides are ruled so that measurements may be made at definite intervals along the length of specimens under observation.

METHOD OF MAKING MEASUREMENTS

The scale of the micrometer eyepiece is conveniently calibrated by comparison with a stage micrometer which is ruled on a glass slide. The calibration factor is dependent on the

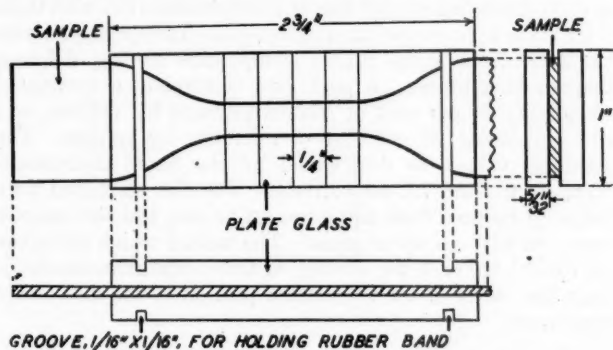


FIGURE 2. SPECIMEN HOLDER OF GLASS PLATES HELD TOGETHER WITH RUBBER BANDS

length of the draw tube of the microscope, and consequently may be adjusted to a convenient number by the proper setting of the draw tube. In the case of the equipment described herein, the calibration factor for the 32-mm. objective ranges from 0.0373 mm. per scale division for a 150-mm. tube length, to 0.0470 mm. for a tube length of 170 mm., and has the convenient value, 0.0400 mm. per scale division, when the tube length is adjusted to 161.7 mm.

In making measurements, the specimen under examination is mounted in a holder and located in the middle of the microscope field with the proper focus, at which the scale and the surface of the specimen appear in the same plane and show no relative displacement as the eye is moved from one side of the eyepiece to the other. The eyepiece is then rotated so as to bring the scale across the specimen in the direction in which measurement is desired. If the edges of the specimen are clean-cut, readings may be estimated to 0.1 scale division, although a reading to 0.5 scale division, which may be made

almost at a glance, is equivalent to a precision of 0.5 per cent if the object covers the full scale. If the sample has been placed symmetrically in the holder, a length of several centimeters may be brought into the field by lateral motion of the mechanical stage. This permits the cut edges to be scrutinized for irregularities, and facilitates the making of measurements at a number of points along a strip.

The microscope may be readily employed for examining and measuring the dimensions of a die. It is only necessary to remove the stage and mirror and mount the die in the field of vision. The difficulty of focusing sharply on the edges of the die may be obviated by placing a glass slide across the die and bringing the lower surface of the glass into focus by observing marks on it.

ILLUSTRATIVE MEASUREMENTS

Measurements of the width of the constricted portion of several dumb-bell shaped dies and of specimens cut with them were made by means of the microscope. The specimens were prepared from three rubber compounds having different degrees of hardness: a pure gum compound, a compound containing 24 per cent of titanox pigment by volume, and one containing 20 per cent of micronex by volume. The hardness values, as determined by the Shore instrument, were 48, 60, and 75, respectively. The dies employed were taken at random from those in routine use, and the samples were cut with an arbor press. The widths which are given in Table I are each the average of three measurements made near the center of the constricted portion of the dies or the specimens.

TABLE I. WIDTH OF RUBBER TEST SPECIMENS AND DIES

OBJECTS MEASURED	POSITION	WIDTH			
		Die 1	Die 2	Die 3	Die 4
		<i>Mm.</i>	<i>Mm.</i>	<i>Mm.</i>	<i>Mm.</i>
Dies		6.58	6.43	6.54	6.45
Micronex rubber samples	Top	6.68	6.44	6.48	6.48
	Bottom	6.68	6.48	6.48	6.38
Titanox rubber samples	Top	6.64	6.46	6.48	6.48
	Bottom	6.84	6.74	6.72	6.55
Pure gum rubber samples	Top	6.64	6.46	6.49	6.50
	Bottom	6.82	6.68	6.69	6.58

The results indicate that the specimens are on the average wider than the die with which they were cut, the upper side being about the same width as the die, but the lower side being appreciably wider in the case of the softer compounds. The mean of the top and bottom widths was in several instances as much as 0.10 to 0.15 mm. greater than the width of the die, hence the possible error which might arise from this source would be of the order of 2 per cent if the width of the test specimen were assumed to be the width of the die. This estimate leaves out of consideration the fact that the edges of specimens cut with a die are usually somewhat concave.

At the time of measurement, however, it is possible to make qualitative observation of the degree of concavity.

Measurements of thickness were made with the microscope on some of these same specimens, mounted on edge in a slot in a wooden block. A comparison of the values found with the thickness as indicated by a dial gage of the plunger type is given in Table II. This gage was provided with a contact foot 6.4 mm. (0.25 inch) in diameter, and was actuated by a load of 85 grams (3 oz.). In the case of the soft, pure gum stock, the thickness indicated by the microscope was of the order of 2 per cent greater than the thickness indicated by the gage, as would be expected from the evident compression by the contact foot. In the case of the stiffer stocks, the measurements by the microscope and the gage were in reasonably close agreement. In some instances the thickness indicated by the gage was somewhat the greater. This may have been owing in part to bloom and dust particles on the surface of the specimens.

TABLE II. COMPARATIVE MEASUREMENTS OF THICKNESS

SPECIMEN	THICKNESS	
	By microscope Mm.	By plunger type gage Mm.
Pure gum	1 2.13	2.08
	2 2.06	2.02
	3 2.08	2.05
	4 2.07	2.04
Titanox	1 1.40	1.40
	2 1.34	1.35
	3 1.41	1.42
	4 1.32	1.33

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